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Naval Surface Warfare Center**

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**Evaluation of Hydroxyethane  
Diphosphonic Acid (HEDPA)as Metal  
Cleaning Agent Using Chemical and  
Electrochemical Test Methods: Part II**

by

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**Evaluation of Hydroxyethane Diphosphonic Acid (HEDPA) as**  
**Metal Cleaning Agent Using Chemical and Electrochemical Test**  
**Methods: Part II**



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## ABSTRACT

In order to evaluate the adaptability of hydroxyethane diposphonic acid (HEDPA) as an environmentally benign alternative rust removal agent, a systematic investigation is being carried out. The effectiveness of HEDPA was thoroughly investigated as a function of acid concentration in the range 2 -100 vol% and at different temperatures in the temperature range 27 – 60°C.

The results suggest that the acid HEDPA is very effective in the rust removal process. The rate of rust removal by HEDPA is strongly dependent on the acid concentration and the solution temperature. Once an optimum threshold is reached further increase in either the acid concentration and/or temperature has a negative effect on the reaction kinetics. While the rust was completely removed by the 2 vol% HEDPA within 3 hours at 27°C, the rust removal was completed within 30 minutes of treatment at 60°C. Similarly, while, the complete rust removal by 2 vol% HEDPA was noticed after 3 hours, 10 vol.% HEDPA required chemical treatment for 0.75 hours at 27°C. However, chemical treatment with as received 100 vol% HEDPA did not dissolve even 20% of the rust after 6 hours and the rust removal at 60°C was < 2 %. Chemical treatment of rusted steel samples with concentrated HEDPA solution (concentration range 5 – 100 vol.% HEDPA) has produced rust free steel samples with very rough surface topography. In addition, the chemical processing at higher temperatures (40 – 60°C) and higher HEDPA concentrations (5-100 vol.%) produced strong pungent smell and unpleasant cleaning environment. The most effective HEDPA concentration and temperature for the rust removal appears to be 2 – 4 vol% and < 40°C respectively.

The activation energy for the rust dissolution process also appears to increase with an increase in the acid concentration. However, it appears that the increase is not very significant for the concentrations in the range 2 - 4 vol% HEDPA (2 vol% - activation energy  $11 \pm 1$  kcal/mole; 3 vol. % - activation energy  $12 \pm 3$  kcal/mole and 4 vol% - activation energy  $14 \pm 2$  kcal/mole). The activation energies for rust dissolution by 5, 10 and 20 vol% HEDPA were found to be 20, 28 and 32 kcal/mole. Above, 20 vol% HEDPA concentrations, a semi-quantitative determined value for the activation energy is  $\sim 2 \pm 2$  kcal/mole.

Prolonged treatment of samples with HEDPA allows the re-deposition of the reaction products onto the cleaned sample surface. The reaction product contains a mixture of various higher order iron phosphates.

## **ADMINISTRATIVE INFORMATION**

This report of research during the period of FY 98 was funded by the CDNSWC Independent Research Program (ILIR), sponsored by the Office of the Naval Research, ONR 10, and administered by the Research Director, CDNSWC 0112, Dr.Bruce Douglas, under the program element 61152N , Task Area ZR-000-01-01 and the CDNSWC Work Unit 1-6120-149. This work was supervised within the Metals Department (Code 61) by Dr. L. F. Aprigliano (Code 612) and Mr. R. J. Ferrara (Code 613).

## **INTRODUCTION**

The development of new materials with improved hot water and salt water corrosion resistance is very important. As these materials are being proven, it is also important to develop procedures and methods to maintain the existing materials currently in use. Advanced technological maintenance processes would have applications in several areas, viz. the electric utility communities, for the removal of deposits from the thermal power plant equipment, and in the civilian and military ship building industry where the removal of corrosion products from ship platforms, on-board tanks, etc. is necessary. Recent trends in the industrial and military sectors emphasize a mandated cost savings on material acquisition results in reduced regular equipment purchases. Therefore, it is even more important to extend the operational life of the presently available systems. In addition, the effects of new environmental policies on maintenance processes have to be considered.

The common classical rust and/or paint removal methods are based on the use of inorganic abrasive grits. This is changing to the use of organic grits, fine dry ice particles, and, most recently, the use of high power water jet blasting to clean the surfaces. These procedures do offer logistical advantages in the removal process, but the operational labor tends to be costly. An alternative approach that is less labor intensive would be to apply an environmentally acceptable solution that will dissolve the contaminants within a reasonable time and be easily flushed from the surface, resulting in an acceptably cleaned surface.

Freshly cleaned surfaces would then require an additional preservation step in order to minimize new corrosion. The preservation is often done by applying an organic paint coating to the freshly cleaned surfaces. If the corrosion product removal by inferior chemical agents has left chemical residue on the surface of the metal, the residue may weaken the metal - paint adhesion and bonding. Therefore, a technical challenge is to develop an environmentally acceptable recipe that removes the corrosion products from the existing aged surfaces without leaving a chemical residue harmful to the adhesive nature of the preservation coatings on the cleaned surface.

This project was undertaken to demonstrate cost effective alternative technology for the removal of the corrosion products in on-board ship tanks, on functional mechanical components and on structural components while converting these corrosion product waste into an environmentally acceptable disposable waste. The technology

was introduced to the NSWC CD by personnel from the Argonne National Laboratory (ANL) with an initial intent of providing a method for cleaning radioactive contaminated components [1-3]. However, it was found that this technology can also be extended to remove conventionally contaminated (i.e. rusted) steel surfaces. Compared to the present conventional cleaning systems, the environmentally acceptable chemical cleansing procedures have a potential of offering lower ship maintenance costs. This cost benefit is the result of a lower clean-up time, accessibility of liquids and the environmentally acceptable disposability of the chemical reagents after the clean-up effort.

The overall program has two objectives: (1) to provide basic scientific information of the chemical and electrochemical interactions at the metal - chemical reagent interface during corrosion product removal, and (2) to determine the adhesion and bonding characteristics of a protective organic coating applied to the cleaned steel surface. The specific technical tasks that will be addressed are :

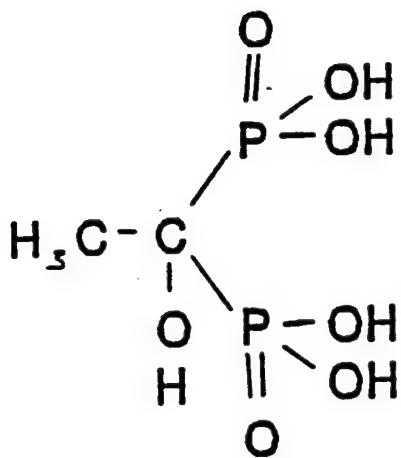
- a). to follow and model the kinetics of the removal of corrosion products and characterize the microstructure and morphology of the cleaned surface;
- b). to coat the cleaned metal surface with an organic coating and study the adhesion and bonding characteristics, and
- c). to test the electrochemical and corrosion characteristics of the coatings in the laboratory using the conventional chemical methods and the electrochemical impedance spectroscopy (EIS) technique.

The present research effort concentrated on (a) determining the chemical kinetic process parameters for the rust removal process as a function of solution concentration and the reaction temperature; (b) characterizing the microstructure and morphology of the cleaned metal surface; (c) determining the electrochemical characteristics of the metal-solution interface during the rust removal process (using the conventional and electrochemical impedance spectroscopy (EIS) techniques); and d) modeling the mechanism of the rust removal process in terms of the chemical kinetic and electrochemical kinetic parameters.

In this report, the complete results obtained for this new class of rust removing chelating agent are being presented following the chemical kinetic and x-ray diffraction studies.

The reagent, 1-hydroxyethane-1,l-diphosphonic acid (HEDPA, also referred to as alkylphosphonic acid), is a water soluble liquid and has general physical characteristics similar to water. The chemical structure of the HEDPA is shown in Figure 1.

The hydroxyethane diphosphonic acid has two phosphate groups and one extra hydroxyl (-OH) group, indicating that the iron in Fe 2+ and or Fe3+ state can compound with free hydroxyl (-OH) group and/or with the (P=O) cation sites and /or with the (P-OH) cation site. A brief description and the details of the inception of this program were reported earlier [4].



1-hydroxyethane-1,1 diphosphonic acid

HEDPA; C<sub>2</sub>P<sub>2</sub>O<sub>7</sub>H<sub>2</sub>; MW = 206.02

Alkylphosphonic acid

IonQuest 201 (Albright & Wilson)

Figure 1. The chemical structure of 1-hydroxyethane-1,1 diphosphonic acid (HEDPA).

Phosphoric acid treatment of steel surfaces has been shown to improve the adherence of subsequently applied paint systems [5]. As the HEDPA is phosphorus based, the likelihood that the coating would serve in a similar fashion to a phosphated surface seemed possible. Therefore, this investigation was undertaken to study the use of HEDPA for cleaning of rusted steel.

### THEORETICAL

Two generally accepted mechanisms for the dissolution of metal oxides are reported in the literature [6-11]. The first is referred to as the adsorption mechanism [6,7] and the second is referred as the electrochemical theory [8-11]. Based on the electrochemical considerations it was suggested in the literature that the overall rate of dissolution of rust can be expressed as:

$$(d\alpha/dt) = k \{(a_{H^+}^{0.5})(a_{Fe^{+2}}^{0.5})(a_{Fe^{+3}}^{-0.5})\} \quad \text{----- (Eq.1)}$$

where “ $\alpha$ ” is the fraction of metal species dissolved, “ $a$ ” the activity of acid, metal ion species and “ $k$ ” the rate constant. For rust removal, the potential for the acid to dissolve iron species is determined by the reaction



From equations (1) and (2) it can be suggested that by lowering the  $(Fe^{+3}/Fe^{+2})$  ratio, the rust removal process can be accelerated. If one assumes that the kinetics of the rust

removal is a chemically controlled process, (i.e the rate limiting step is the surface reaction), the rate of rust removal can be expressed as [5-6]

$$[1 - \{1 - \alpha\}^{1/3}] = k't \quad \text{----- (Eq.3)}$$

where  $k'$  is the kinetic constant and  $t$  is the reaction time.

Although the above models can predict the dissolution kinetics of rust particles in HEDPA, the above models may not be applicable for predicting the rust dissolution from a large surface of rusted steel. In order to account for the effect of large surface area on reaction kinetic modeling, a new model was developed. In this approach, it is assumed that the rust removal process proceeds as in a 2 - dimensional reaction. However, the reaction zone covers the entire surface area of the sample. The surface species first forms a new and active nuclei which is dissolved by the HEDPA. The overall rate of rust removal can then be expressed as [7-10]

$$\ln[\alpha/(1-\alpha)] = k''(t - t_i) \quad \text{----- (Eq.4)}$$

where  $k''$  is the rate constant and ' $t_i$ ' the time for the termination of the accelerated rust removal sequence.

In order to determine the chemical reaction rates of different processes involved in the rust removal, an alternative model was developed. This model is based on the assumption that the rust removal by hydroxyethane diphosphonic (HEDPA) acid is a solid state reaction process.

The overall (iron oxide dissolution) chemical reaction involves (a) removal of oxide (b) removal of pure metal; and (c) re-precipitation of metal complex. Therefore, it is

justifiable to assume that the kinetics of the reaction process depend on both the acid concentration and the reaction temperature. Figure 2 shows a schematic representation of typical rust removal process in which several chemical activities may occur; such as the chemical reaction between (i) the sample oxide phase, (ii) both oxide and metal phase, (iii) only metal phase and possible adsorption of the reaction by product on to the metal surface, (iv) only the adsorption of reaction by product and or products and (v) the re-dissolution of the adsorbed precipitate and its re-adsorption.

A theoretical analog for the reaction kinetics process can be suggested as follows : For convenience, assuming that only the first three phases are predominant during rust removal process by HEDPA acid, as the reaction progresses, the overall weight change with time can be represented as

$$(dW/dt) = - A \{ (dW_{oxide}/dt) + (dW_{metal}/dt) - (dW_{ppt}/dt) \} \quad (5)$$

where A = kinetic constant

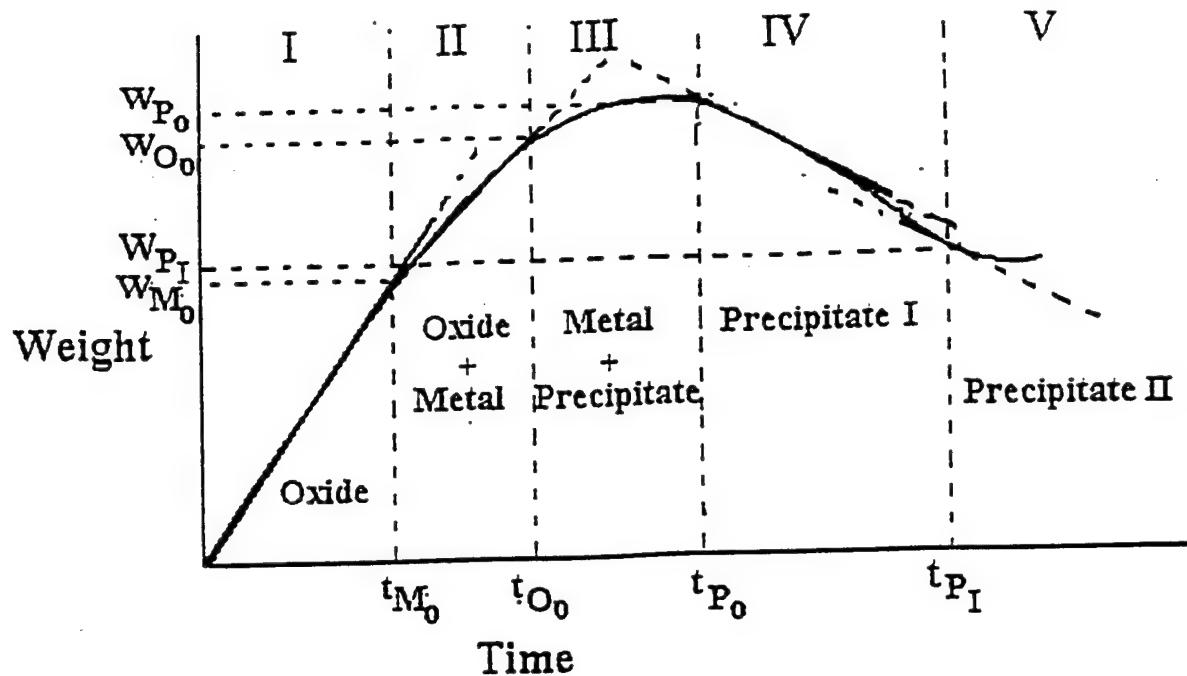
$(dW/dt)$  = rate of sample weight change

$(dW_{oxide}/dt)$  = rate of oxide dissolved

$(dW_{metal}/dt)$  = rate of metal dissolved and

$(dW_{ppt}/dt)$  = rate of re-precipitation

An initial assumption is that the steel surface is "completely" covered by an oxide, i.e., no unoxidized iron is available for the chemical reaction. Once the rusted steel is exposed to the acid and the chemical reaction starts (reaction time ( $t$ ) = 0) the HEDPA reacts only with the oxide layer (Region I). After a certain time, the bare metal becomes



Region I Only Oxide Layer is being Removed

Region II Both Oxide and Pure Metal Layers are Removed

Region III No Oxide & Metal is being Removed and  
Precipitate Starts to Form on the Surface

Region IV No Metal is Removed and Only Reprecipitation

Region V Precipitate Redissolves and Form New Complex

$W_{O_0}, t_{O_0}$  Weight change due to dissolution of metal and also  
reprecipitation of the reaction product; weight at  
which no oxide is present and corresponding time,

$W_{M_0}, t_{M_0}$  Critical weight at which metal starts to dissolve and  
corresponding time,

$W_{P_0}, t_{P_0}$  Critical weight at which no metal is dissolved and  
corresponding time, and

$W_{P_I}, t_{P_I}$  Critical weight at which the initial precipitate starts  
to redissolve due to the formation of new complex  
and corresponding time.

Figure 2. Schematic representation of typical rust removal process.

exposed and, the acid interacts with both the metal and the decreasing quantity of oxide (Region II). Once a critical time is reached the dissolution process tends to be slow (Region III). At this stage, the re-precipitation of the reaction products onto the cleaned metal surface occurs and/or the reaction "by product" may form a complex with the acid in solution and even change the acid concentration (Region III).

Let  $W_{O_0}$ ,  $t_{O_0}$  be the weight change due to dissolution of metal and also re-precipitation of the reaction product (no oxide is present) and its corresponding time,  $W_{M_0}$ ,  $t_{M_0}$  are the critical weight at which metal starts to dissolve and its corresponding time,

$W_{P_0}$ ,  $t_{P_0}$  are critical weight at which no further metal is dissolved and its corresponding time, and

$W_{P_I}$ ,  $t_{P_I}$  are the critical weight at which the initial precipitate starts to redissolve (perhaps due to the formation of new complex) and its corresponding time.

Since in the region I only rust is removed and the change in acid concentration depends upon the net weight loss of the rust, the generalized kinetic expression (Eq. 5) can be rewritten as

$$(dW/dt) = - A (dW_{oxide}/dt) \text{ and } (dW_{metal}/dt) \approx (dW_{ppt}/dt) = 0 \quad (\text{Eq. 6})$$

Initially, the change in the acid concentration is small; therefore, the order of the overall chemical reaction with respect to the acid concentration can be approximated as zero order. The integral form of the rate process, then, can be expressed as

$$K_{R(I)} t = W + \text{Const.} \quad [\text{Limits : } t_0 \rightarrow t_{M_0}; 0 \rightarrow W_{m_0}]$$

$$k_O t = W + \text{Const.} \quad K_{R(I)} \approx k_O \quad (\text{Eq. 7})$$

However, in region II, both the oxide and metal are being removed by the acid.

Therefore the order of the reaction with respect to the acid concentration can be approximated as a second order reaction

$$(dW/dt) = - A \{ (dW_{\text{oxide}}/dt) + (dw_{\text{Metal}}/dt) \} \quad (\text{Eq. 8})$$

and the integral form can be expressed as

$$k_{R(II)} = \{W/W_0\} (W_0 - W) \quad (\text{Eq. 9})$$

where  $W_0$  is the total weight of oxide and the metal removed in region II and

$$\text{and } k_{R(II)} t = \{k_O \cdot W_{\text{oxide}} + k_M W_{\text{metal}}\};$$

$$W_{\text{oxide}} \approx W_{\text{metal}} \approx (1/2) \{W_{O_0} + W_{M_0}\} \quad (\text{Eq. 10})$$

where  $W_{O_0}$ ,  $W_{M_0}$  are the critical weights after which no oxide and metal was removed

$$k_{R(II)} t = [(1/2) \{k_O + k_M\} \{W_{O_0} + W_{M_0}\}] \quad (\text{Eq. 11})$$

In region III there is no oxide to be dissolved and the acid reaction takes place at the metal acid interface. In addition depending upon the conditions of the reaction, the reaction products are re-precipitated. When such a situation arises, the rate of weight loss can be represented as

$$(dW_{R(III)}/dt) = - A \{ (dW_{\text{metal}}/dt) - (dW_{\text{ppt}}/dt) \} \quad (\text{Eq. 12})$$

In region III also it can be approximated that with respect to the acid concentration, the order of the reaction is second order and integral form can be expressed as

$$k_{R(III)} t = \{k_M W_{\text{metal}} - k_{\text{ppt}} \cdot W_{\text{ppt}}\} \quad (\text{Eq. 13})$$

If one assumes that in region III

$$W_{\text{oxide}} \approx 0; W_{\text{metal}} \approx (1/2) \{W_{O_0} + W_{P_0}\} \text{ and } W_{\text{ppt}} \approx (1/2) \{W_{P_0} + W_{P_I}\};$$

(where  $W_{P_0}$  and  $W_{P_I}$  are the critical weights at which neither oxide nor the metal is removed and the precipitate start forming, respectively), the kinetic expression shown above (Eq. 13) can be rewritten as follows.

$$k_R(\text{III}) = (1/2) \{k_M \{W_{O_0} + W_{P_0}\} - k_{\text{ppt}} \cdot \{W_{P_0} + W_{P_I}\}\} \quad (\text{Eq. 14})$$

The kinetic parameters for the rust removal process thus can be determined as a function of both HEDPA concentration and reaction temperature. The above proposed model indicates that once most of the oxide (rust) is removed, the metal starts dissolving in the acid followed by the re-precipitation of the reaction products onto the surface of the cleaned surface. If one assumed that the rate of rust removal (Region I) is "k1" and the rate of metal and remaining rust removal (Region II) is "k2" and the re-precipitation (Region III) is "k3" respectively, it is possible to estimate the maximum time ( $t_{\max}$ ) required for the completion of each process (Region I – Region II – Region III) as follows:

$$k_1 \qquad \qquad \qquad k_2 \qquad \qquad \qquad k_3$$

Rust Sample  $\rightarrow$  Stage I  $\rightarrow$  Stage II  $\rightarrow$  Stage III

where, Stage I: Sample with Rust

Stage I – II : Sample with no rust and ppt formed

Stage I - II - III: Sample covered with thick Ppt. and/or Ppts.

The change in HEDPA concentration ( $C^*$ ) can be represented as

$$C^* = C_{\text{stage I}} + C_{\text{stage II}} + C_{\text{stage III}} \quad (\text{Eq. 15})$$

Then the rate of change of acid concentration in each stage can be represented as

$$\text{Stage I} = -(\text{dC}_{\text{stage I}} / \text{dt}) = k_1 C_{\text{stage I}}$$

$$\text{Stage II} = -(\text{dC}_{\text{stage II}} / \text{dt}) = k_2 C_{\text{stage II}}$$

$$\text{Stage III} = (\text{dC}_{\text{stage III}} / \text{dt}) = k_3 C_{\text{stage III}}$$

where  $C_{\text{stage I}}$ ,  $C_{\text{stage II}}$  and  $C_{\text{stage III}}$  are the acid concentrations at the corresponding stages.

Assuming that each stage process begins only after a maximum critical time (ie. the concentration function reaches a maximum and finally becomes "Zero"), the maximum time for the reaction process for Stage I - Stage II and Stage I - Stage II - Stage III can be expressed as

$$t_{\max} (\text{stage I - II}) = [\ln(k_1 / k_2)] / (k_1 - k_2) \text{ and}$$

$$t_{\max} (\text{stage I-II-III}) = [\ln(k_2 / k_3)] / (k_2 - k_3) \quad (\text{Eq. 16})$$

From the above equations (Eq. 15 and 16), it is then possible to predict the state of the chemical cleaning of the steel samples with HEDPA.

## EXPERIMENTAL

Two types of conventional low carbon (1020) steel were investigated. The first type was lightly rusted and the second type was heavily rusted. To make the lightly rusted steel samples, conventionally epoxy mounted samples, polished to a 600 grit finish (SiC) for the electrochemical investigations, were placed in the laboratory environment (ca. 25°C, 60% RH) for a minimum of two weeks prior to use. The air-formed oxide film thickness of similarly treated iron/steel has been suggested to be 5 to 6 nm. To make

the heavily rusted type, samples were prepared by suspending steel panels from a fence adjacent to the NSWCCD Annapolis laboratory and the Severn River for a minimum of two weeks. The red rust content was approximately  $30 \text{ mg/cm}^2$ .

A commercial source of HEDPA was used. This reagent Ionquest 201 was supplied by Albright and Wilson, VA. It is a mixture of 60 %w/o HEDPA and 40 wt.% water. It has a solution specific gravity and pH of 1.4 gm/cc and 1.7, respectively. The present evaluation of the rust removal process was performed with a 2 v/o HEDPA that was produced by diluting the as procured Ionquest 201 stock solution. This concentration was selected based on earlier work at ANL. The pH of the 2 v/o solution was approximately 2.2 at  $25^\circ\text{C}$ .

Two types of experiments (weight change determination and x-ray diffraction analysis using copper  $\text{K}_\alpha$  radiation) were performed. Sample weight changes with respect to increasing exposure times were used to evaluate the kinetics of oxide removal from the heavily rusted samples and subsequent formation of a new surface compound. Evaluations at eight solution concentrations and four temperatures between 25 and  $60^\circ\text{C}$  were made to establish the kinetic parameters.

### **RESULTS AND DISCUSSION**

Figures 3(A) – (D) show typical weight change versus time profiles of rusted samples immersed in 2 v/o HEDPA solution and at different temperatures in the range 27 –  $60^\circ\text{C}$ . The solution volume to the sample exposed surface area ratio was maintained at approximately  $25 \text{ cc/cm}^2$ . The results shown in Figures 3 suggest that the rate of weight

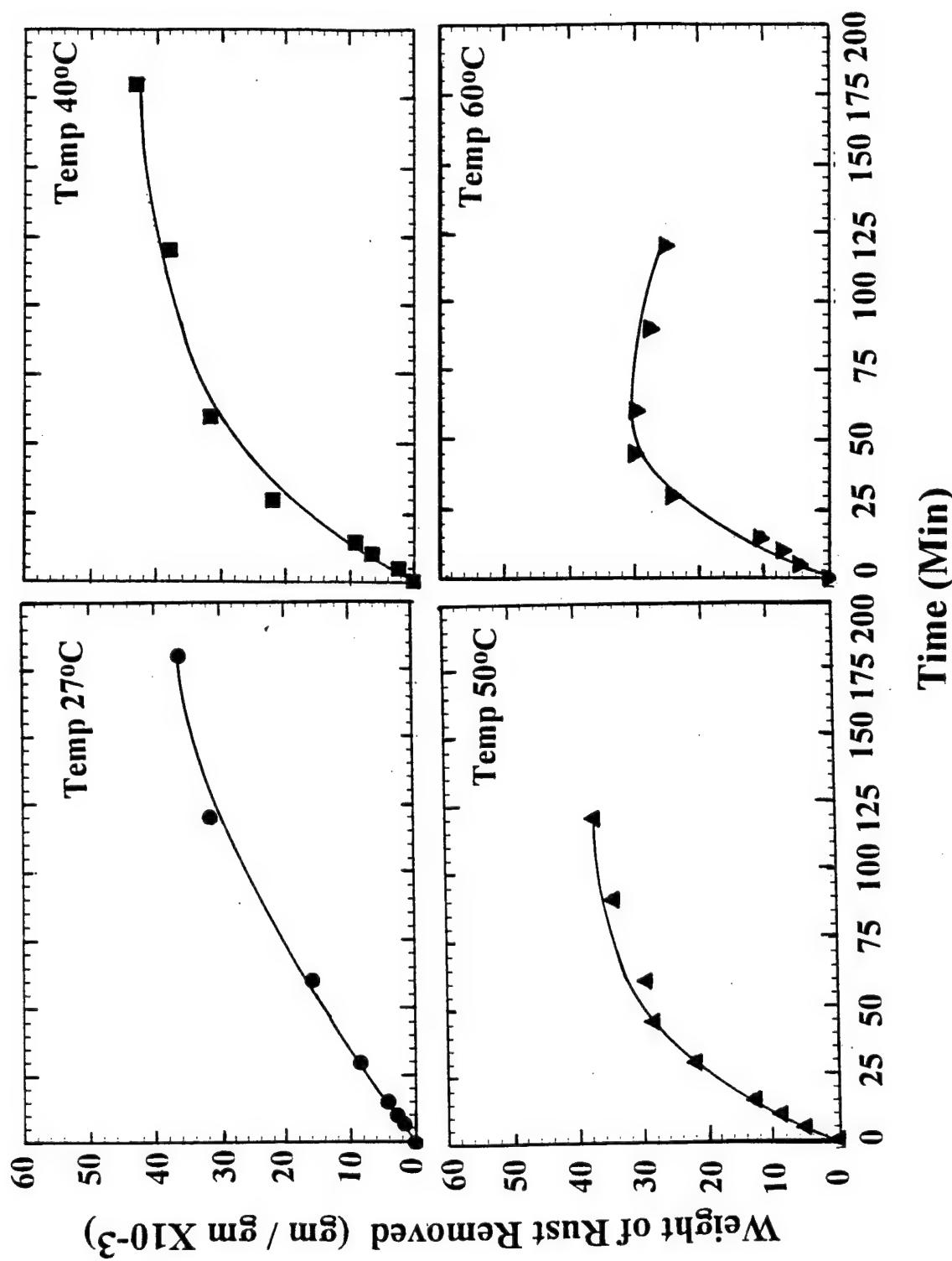


Figure 3. Weight loss versus time plot of rusted steel sample in 2 vol % hydroxyethane diphosphonic solution at 27, 40, 50 and 60°C.

loss initially increases with time and once it reaches an optimum, the weight loss rate decreases and eventually tends to be zero. An increase in the solution temperature accelerates the reaction. At higher temperatures the weight loss versus time profiles show a weight gain due to re-precipitation of the products onto the sample surface.

Figure 4 shows a typical weight loss versus time profile obtained from rusted samples subjected to the chemical cleaning by 2 vol% HEDPA at 40°C. The over all rate of reaction was determined from the initial slope of the weight loss versus time profile. The reaction rates corresponding to different stages of the reaction process (viz. Stage I where in only oxide was removed, Stage II where both oxide and base metal were dissolved by the HEDPA and Stage III where the base metal is removed and some re-precipitation of the chemical reaction product onto the cleaned metal surface has occurred) was then determined from the model. Typical values for the critical time for the termination of accelerated rust removal and the estimated rate constant are given in Table 1 for 2 vol.% HEDPA as a function of temperature. The results suggest that as the reaction temperature is increased, the rate at which rust is removed by the reagent HEDPA increases and the duration for the rust removal time decreases. Similar observations were made for the rust removal at higher HEDPA concentrations.

The kinetic parameters such as the rate of reaction at different stages of the process, the activation energy and the order of the reaction were calculated using the proposed model (given in the previous section). From the critical time for accelerated chemical reaction process, the order of the chemical reaction was calculated. While the values for the rate constant and the activation energy for the chemical reaction process in 2 vol% HEDPA are given in Table 2, the detailed information on the order of chemical

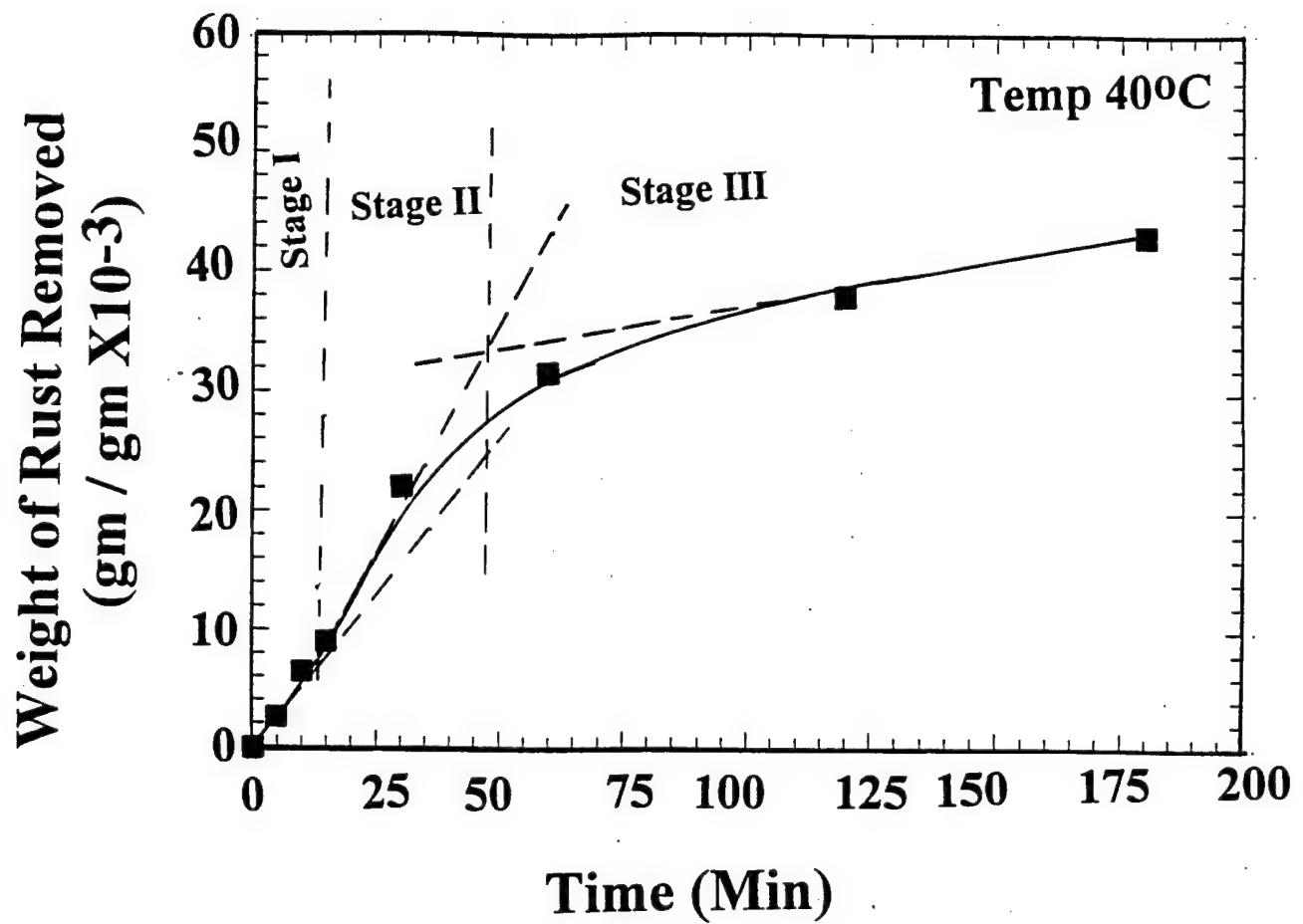


Figure 4. Weight loss versus time plot indicating different stages of chemical stages during the rust removal by 2 vol % HEDPA solution at 27°C.

**Table 1. Experimentally determined rate constants for rust removal process and the time for the termination of accelerated rust removal represented as a function of solution temperature for rust removal process by 2 vol% HEDPA.**

Solution Temperature (C)	T <sub>i</sub> Time for the Termination of Accelerated Rust Removal Time (min)	Rate Constant (per min) X 10 <sup>-3</sup>
27	113 $\pm$ 10	4.3 $\pm$ 0.7
40	53 $\pm$ 10	11.5 $\pm$ 2.5
50	41 $\pm$ 4	13.0 $\pm$ 0.5
60	36 $\pm$ 2	13.5 $\pm$ 0.2

Concentration of Hydroxy ethane di phosphonic acid (HEDPA) : 0.082 M (2 vol.%)

Sample Dimensions : ~ 4 cm diameter X 0.1 cm thick disks

Sample Weight : ~ 11 gm

No. of Samples Measured for Data Reproducibility : 9

**Table 2.** Experimentally determined rate constants for different stages of chemical reaction process represented as a function of solution temperature for rust removal by 2 vo.% HEDPA.

Reaction Temperature (C)	Rate Constant ( $\text{gm cm}^{-2} \text{ min}^{-1}$ ) X $10^{-4}$			
	Overall Process	Stage I	Stage II	Stage III
27	3.2	3.0	2.5	1.0
40	6.7	7.0	4.5	1.0
50	7.1	8.0	5.8	0.9
60	7.8	8.5	7.0	-3.0

Activation energy of the rust removal process :  $11 \pm 1$  kcal/mole

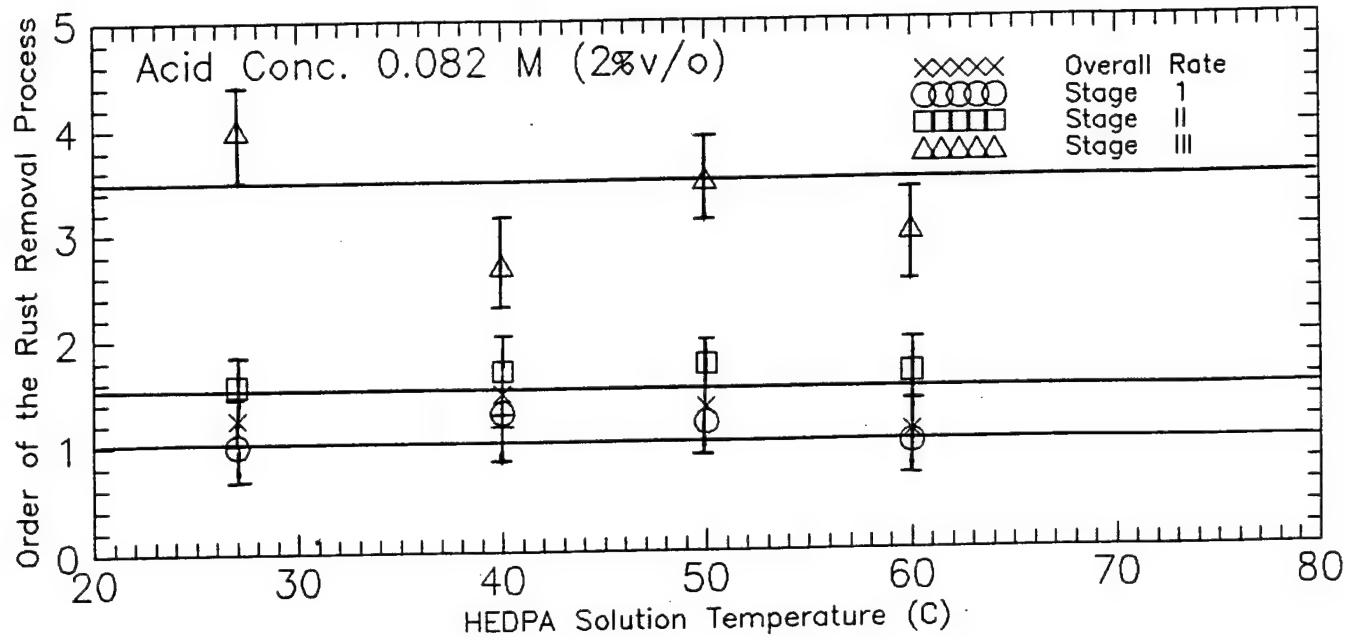


Figure 5. Order of the Chemical reaction versus HEDPA solution temperature plot for rust removal process.

reaction at different stages is shown as a function of solution temperature in Figure 5. The results suggest that with respect to the concentration of the oxide removal, the overall order of the reaction and the order of reaction in the first stage (only oxide is dissolved) is "first order". The order of the reaction in the second stage where some oxide and mostly metal is removed is found to be 1.5, and the order of reaction in the third stage is found to be 3.5 respectively. However the proposed model predicts that the order of reaction for stage II and stage III will be a "second order" (2) and "third order" (3) respectively.

The differences in the initially proposed model and the observed order of chemical reaction process can be explained as follows. The initially proposed model did not consider the chemical reaction independent of diffusion control. Similar differences between the theory and the experimental results can be explained in terms of a diffusion controlled model.

Figures 6 – 13 show typical weight of rust removed versus time profiles obtained during the rust removal by HEDPA at 27°C. From these plots the rate of rust removal and the rates for each different stages of the reaction process were determined using the procedure described earlier. The rate of rust removal at 27°C versus HEDPA concentration is shown in Figure 14. The experimentally determined rate constants (for different stages of chemical reaction process) versus HEDPA concentration and the reaction temperature are given in Tables 3 – 6. The results shown in Figure 14 and Tables 3 - 6 suggest that the effect of HEDPA concentration on the rate of rust removal is significant. For the reagent HEDPA in the concentration range 2 vol% to 20 vol%, the

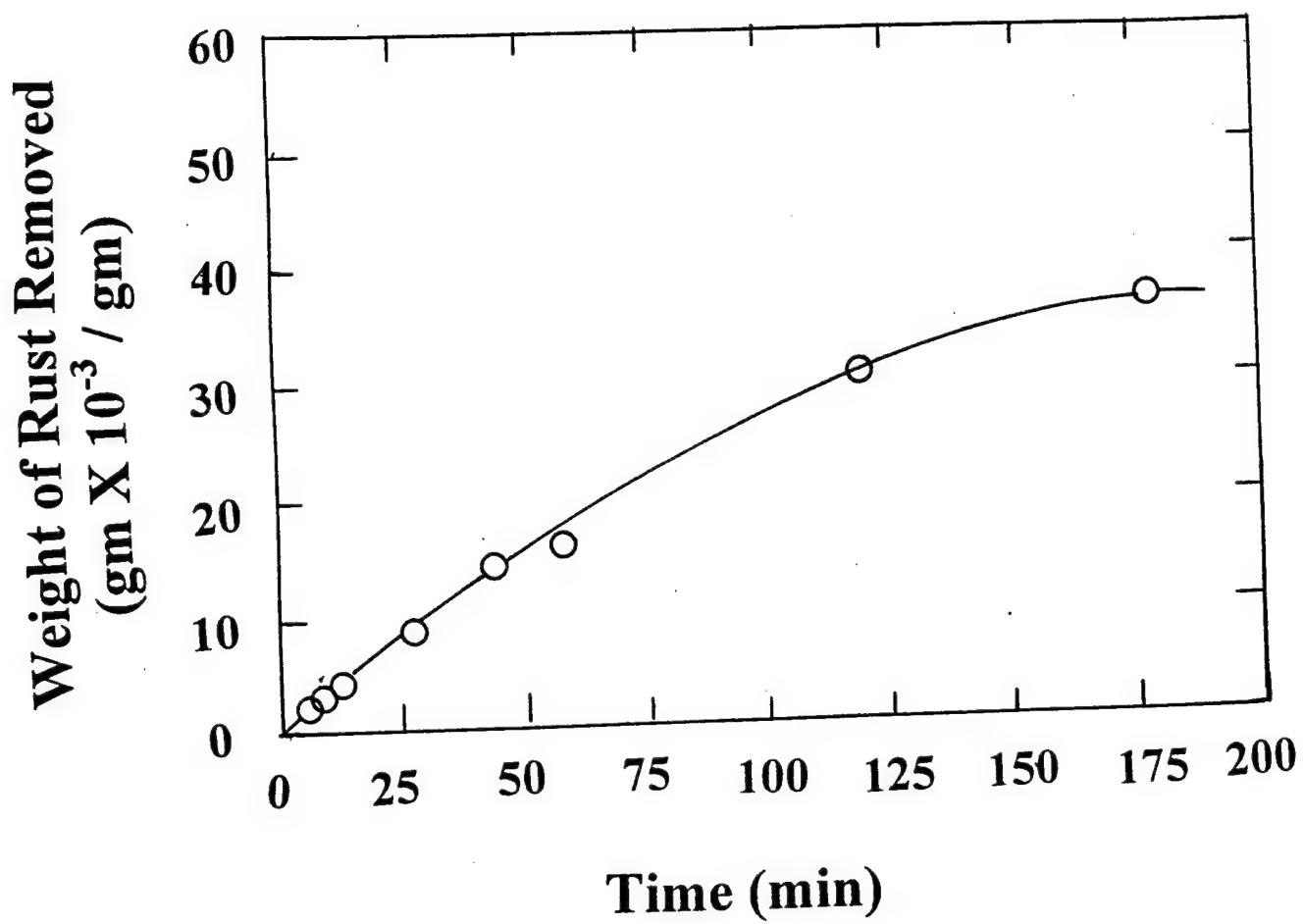


Figure 6. Weight loss versus time plot of rusted steel sample in 2 vol % hydroxyethane diphosphonic acid solution at 27°C.

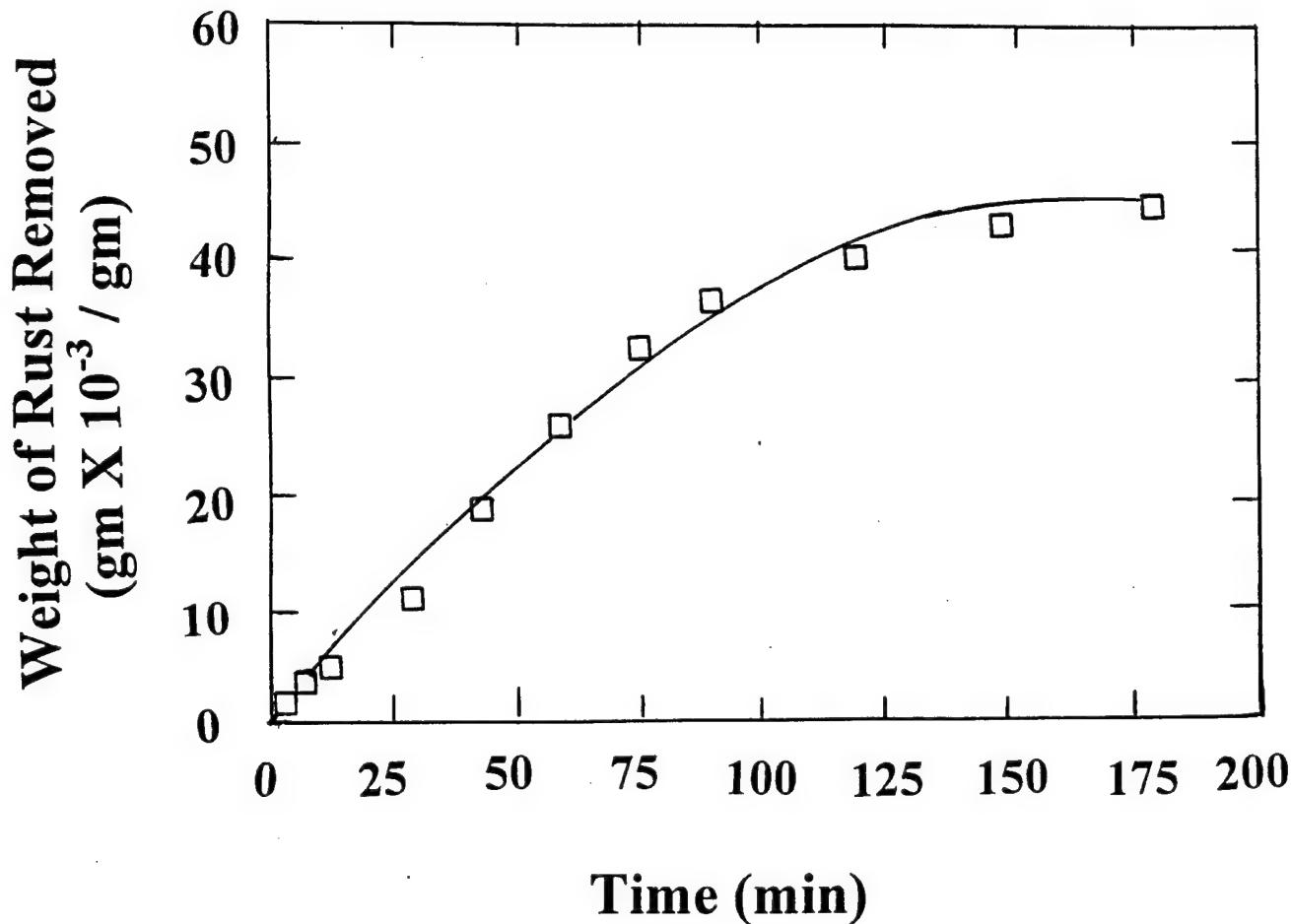


Figure 7. Weight loss versus time plot of rusted steel sample in 3 vol % hydroxyethane diphosphonic acid solution at 27°C.

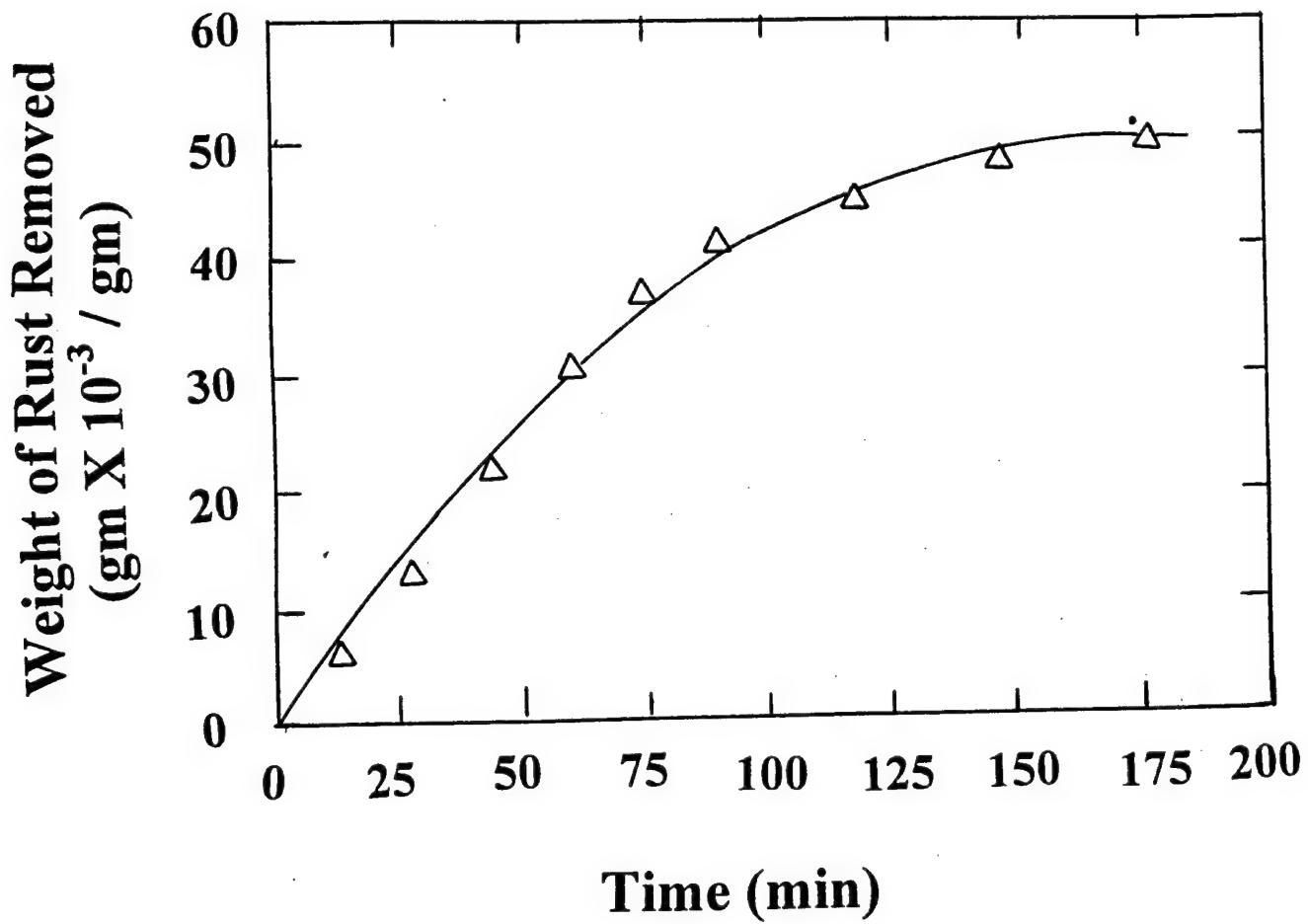


Figure 8. Weight loss versus time plot of rusted steel sample in 4 vol % hydroxyethane diphosphonic acid solution at 27°C

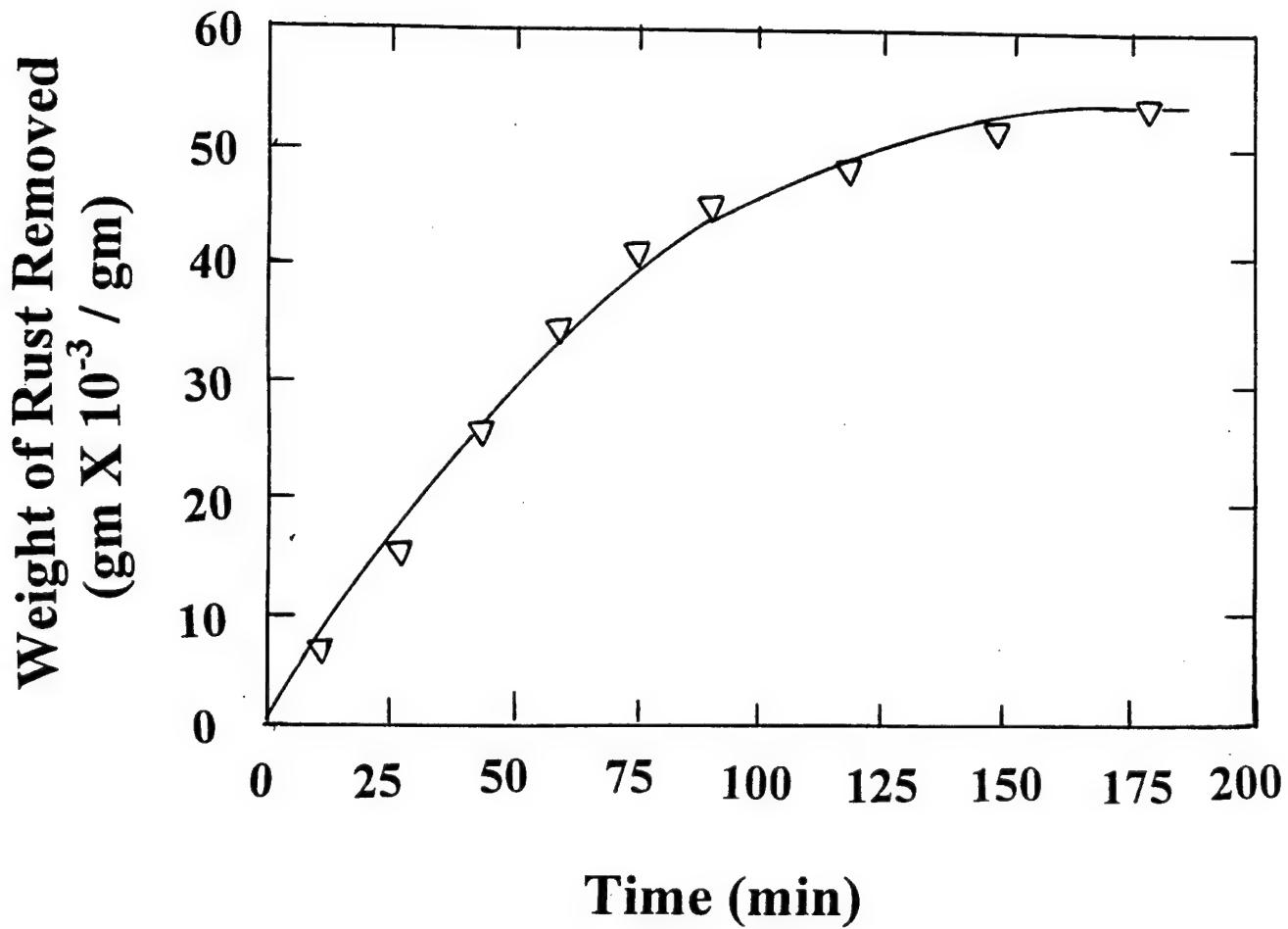


Figure 9. Weight loss versus time plot of rusted steel sample in 5 vol % hydroxyethane diphosphonic acid solution at 27°C.

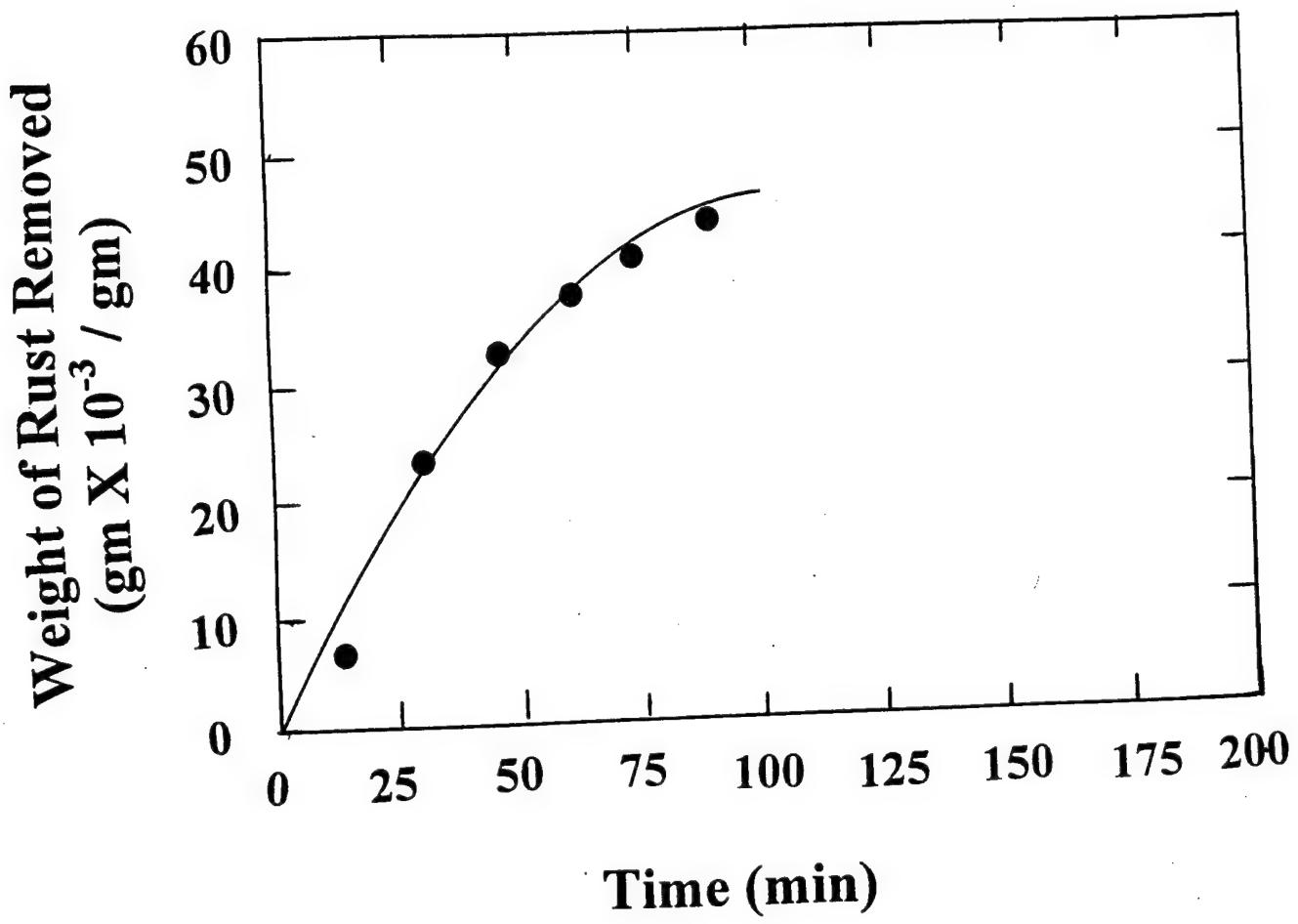


Figure 10. Weight loss versus time plot of rusted steel sample in 10 vol % hydroxyethane diphosphonic acid solution at 27°C.

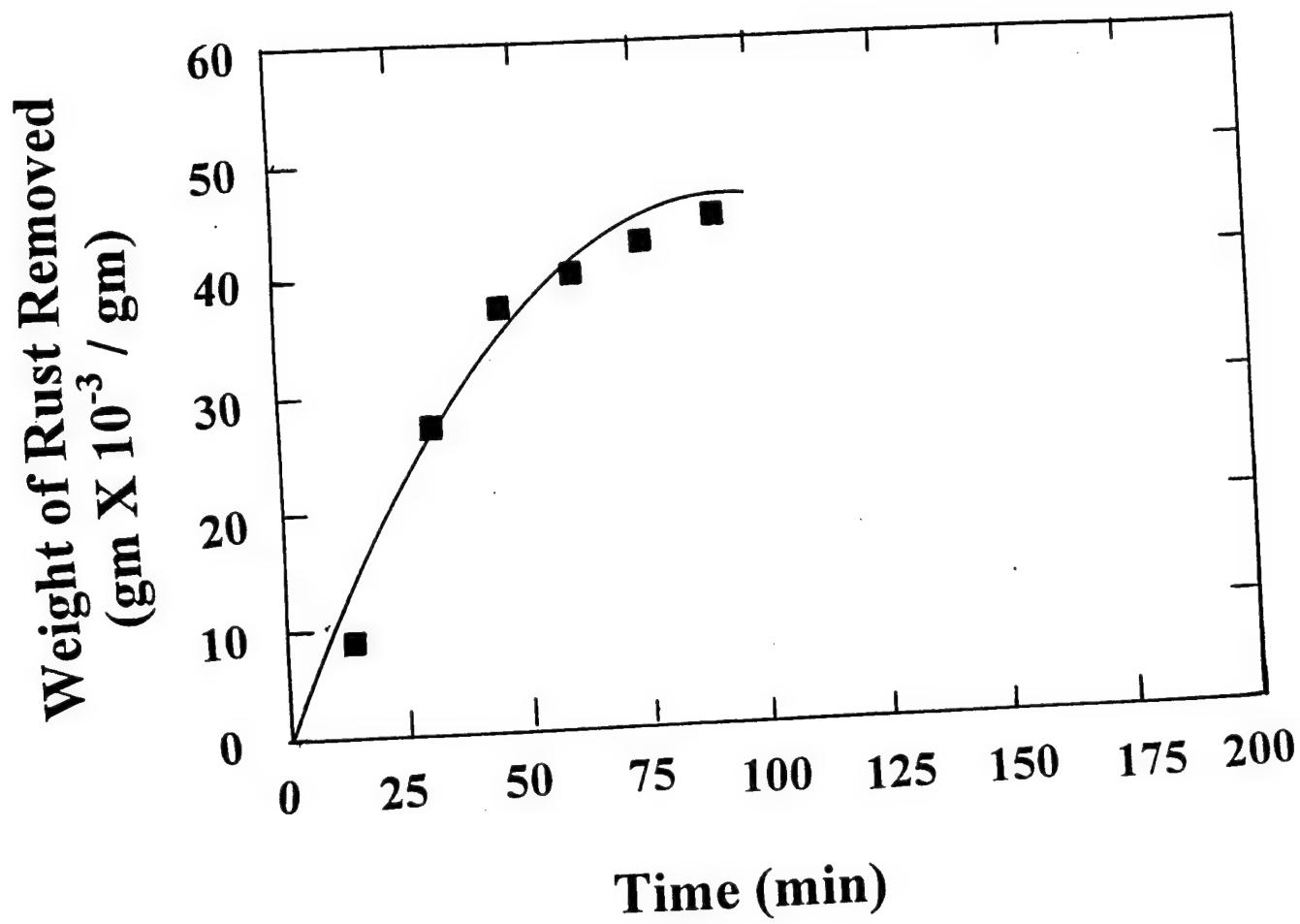


Figure 11. Weight loss versus time plot of rusted steel sample in 20 vol % hydroxyethane diphosphonic acid solution at 27°C.

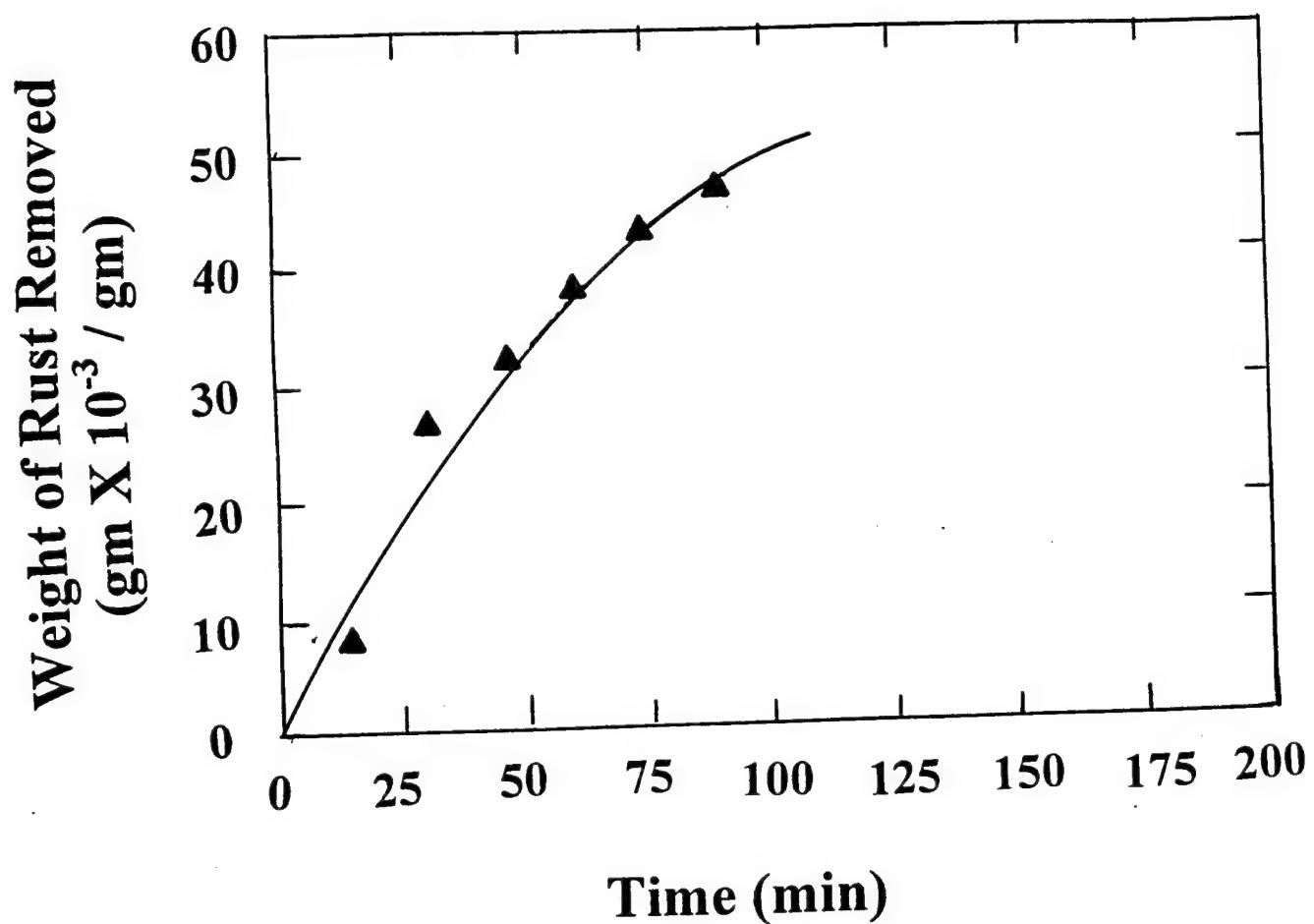


Figure 12. Weight loss versus time plot of rusted steel sample in 50 vol % hydroxyethane diphosphonic acid solution at 27°C.

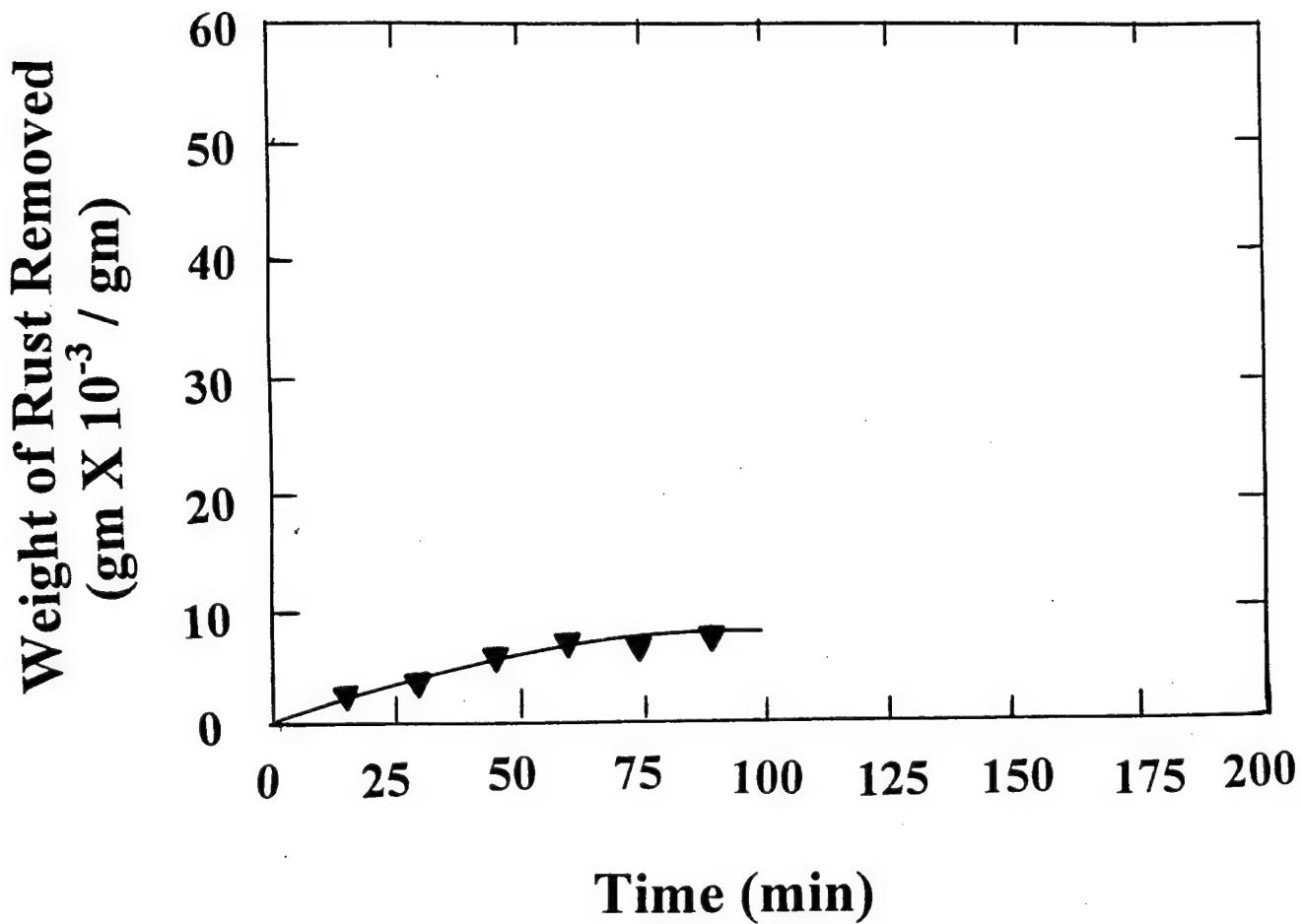


Figure 13. Weight loss versus time plot of rusted steel sample in 100 vol % hydroxyethane diphosphonic acid solution at 27°C.

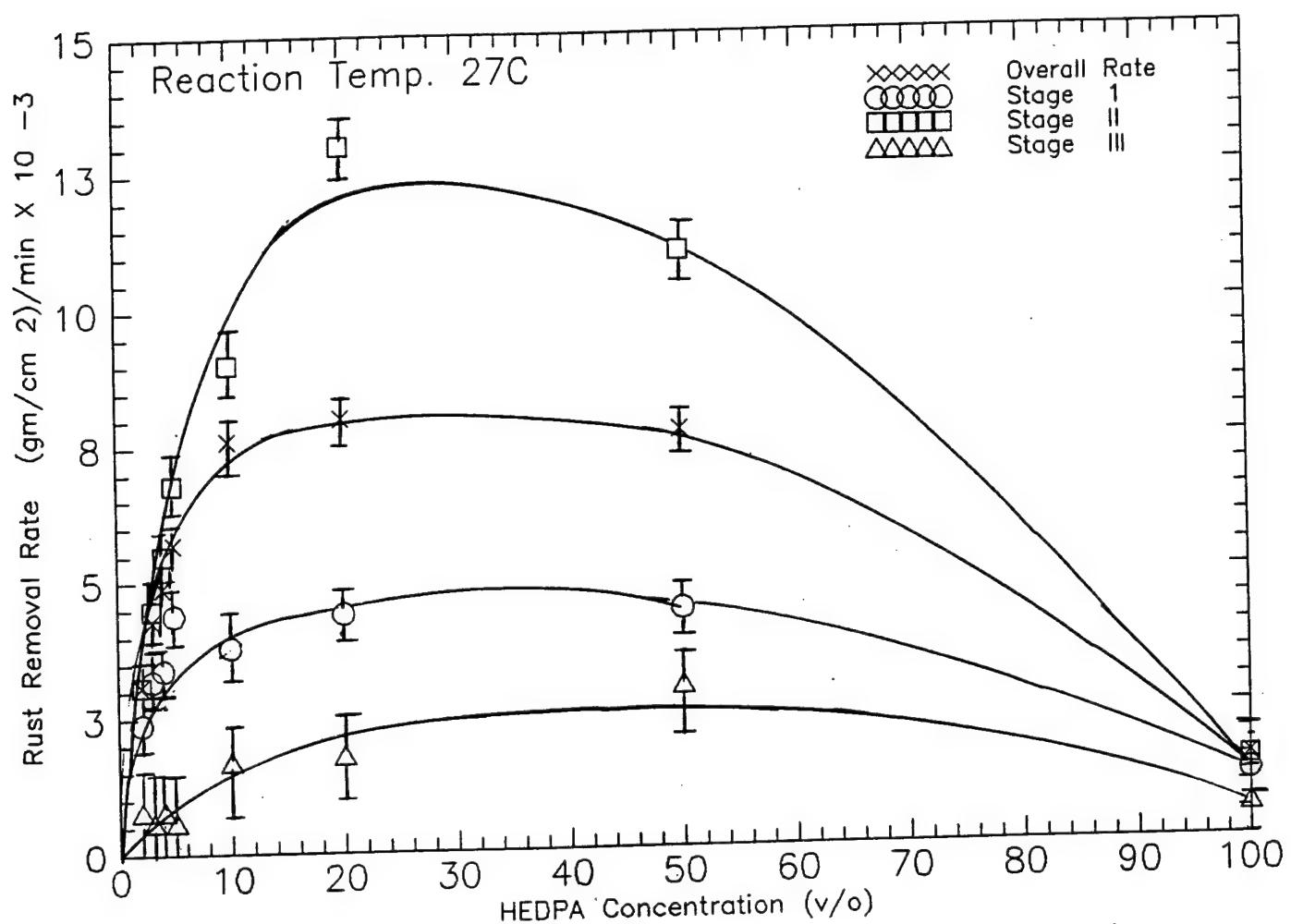


Figure 14. Rate constant versus HEDPA solution concentration plot for rust removal process at 27°C.

**Table 3.** Experimentally determined rate constants for different stages of chemical reaction process represented as a function of HEDPA solution concentration for rust removal at 27°C.

HEDPA Concentration (vol %)	Rate Constant (gm cm <sup>-2</sup> min <sup>-1</sup> ) X 10 <sup>-3</sup>			
	Overall Process	Stage I	Stage II	Stage III
2	0.31	0.24	0.31	0.08
3	0.43	0.32	0.45	0.06
4	0.49	0.34	0.55	0.08
5	0.57	0.44	0.68	0.06
10	0.76	0.38	0.90	0.17
20	0.80	0.44	1.30	0.18
50	0.77	0.44	0.110	0.30
100	0.15	0.12	0.14	0.06

**Table 4. Experimentally determined rate constants for different stages of chemical reaction process represented as a function of HEDPA solution concentration for rust removal at 40°C.**

HEDPA Concentration (vol %)	Rate Constant (gm cm <sup>-2</sup> min <sup>-1</sup> ) X 10 <sup>-3</sup>			
	Overall Process	Stage I	Stage II	Stage III
2	0.67	0.70	0.45	0.10
3	1.2	0.64	1.00	0.17
4	1.48	0.80	1.43	0.21
5	2.20	1.71	2.68	0.23
10	5.30	2.72	6.12	1.04
20	7.12	3.70	11.0	1.5
50	0.83	0.50	1.26	0.34
100	0.153	0.123	0.15	0.062

**Table 5.** Experimentally determined rate constants for different stages of chemical reaction process represented as a function of HEDPA solution concentration for rust removal at 50°C.

HEDPA Concentration (vol %)	Rate Constant (gm cm <sup>-2</sup> min <sup>-1</sup> ) X 10 <sup>-3</sup>			
	Overall Process	Stage I	Stage II	Stage III
2	0.72	0.80	0.58	0.090
3	1.80	1.20	2.60	0.28
4	2.58	1.80	2.90	0.42
5	5.50	4.63	6.70	0.61
10	23.00	11.00	29.00	5.60
20	33.00	17.00	51.00	7.00
50	0.92	0.56	1.39	0.36
100	0.17	0.126	0.14	0.061(?)

**Table 6. Experimentally determined rate constants for different stages of chemical reaction process represented as a function of HEDPA solution concentration for rust removal at 60°C.**

HEDPA Concentration (vol %)	Rate Constant (gm cm <sup>-2</sup> min <sup>-1</sup> ) X 10 <sup>-3</sup>			
	Overall Process	Stage I	Stage II	Stage III
2	0.80	0.85	0.70	?
3	3.80	2.82	3.45	0.52
4	6.00	4.20	7.00	1.00
5	14.20	11.51	17.00	1.51(?)
10	88.00	49.00	100.00	11.00(?)
20	130.00	70.00	51.00	?
50	1.07	0.60	?	?
100	0.165	0.132	?	?

rate at which the rust is removed increases with an increase in the reagent concentration. Above 20 vol%, the above trends are reversed. Similarly, as the solution temperature is increased from 27 – 60°C, the rate of rust removal also increased. However, at higher acid concentrations and solution temperatures, the rate of re-precipitation of reaction products onto the cleaned sample surface also increased.

Figure 15 shows typical order of the chemical reaction versus acid concentration at 27°C. Similar details of the order of reaction at higher temperatures are given in Tables 7 – 14. These results suggest that the order of overall chemical reaction process and stage I is a first order chemical process. The second stage process is 1.5 order process and the third stage is 3.5. The present model predicted values of 1, 2 and 3 for the overall and Stage I process, Stage II process and Stage III process. These differences can be explained as follows. While the theory did not consider any diffusion process involvement during the rust removal, some diffusion controlled mechanism was involved during the actual rust removal by HEDPA. It has to be pointed out that the determination of order of chemical reaction for rust removal by 100 vol.% HEDPA was difficult and the measurement errors were significant. Therefore, in Table 14 the value for the order of reaction was represented with (?).

The activation energy for the rust removal process was calculated using the chemical rate constants shown in Tables 3-7 and the results are shown in Table 15. The results suggest that the energy of activation remained independent of HEDPA concentration in the range 2 – 4 vol.%. However as the acid concentration is increased above 4 vol%, an increase in the reagent concentration has a significant effect on the

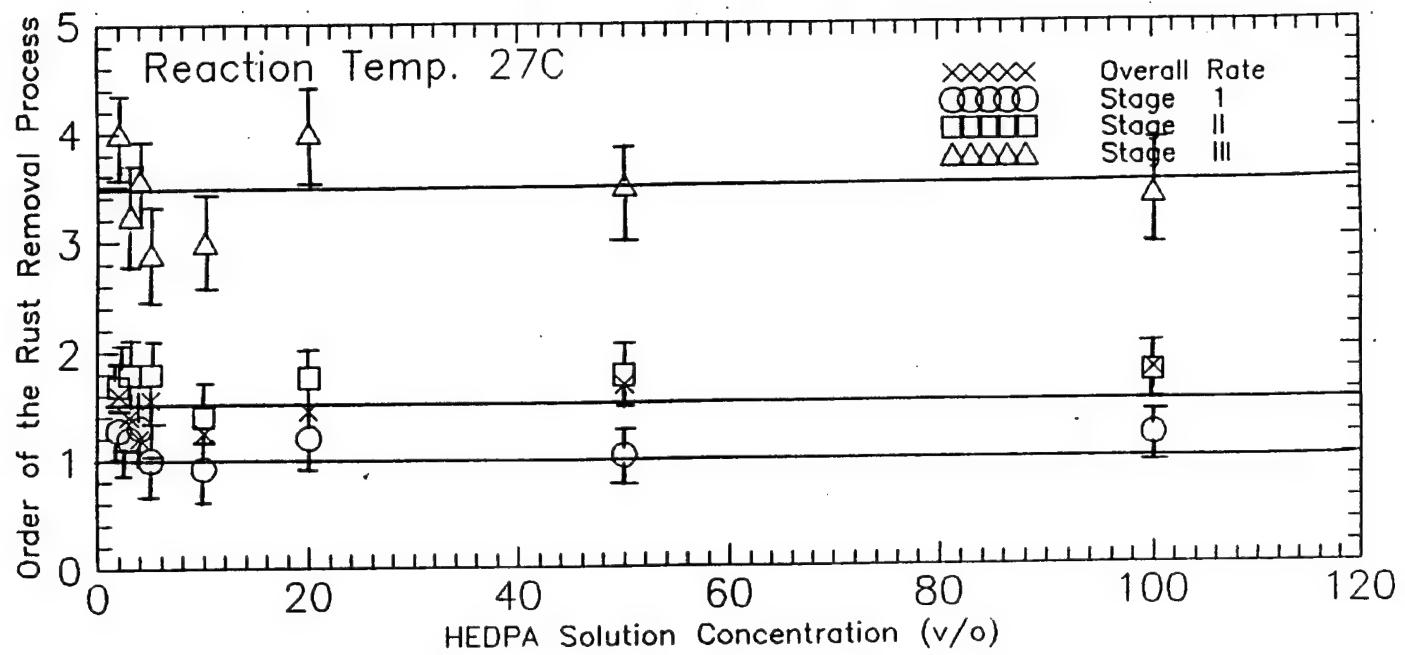


Figure 15. Order of the Chemical reaction versus HEDPA solution concentration plot for rust removal process at 27°C.

**Table 7. Order of the chemical reaction for each stage of chemical transformation during rust removal by 2 vol% HEDPA at different solution temperatures.**

Solution Temperature (C)	Order of the Chemical Reaction			
	Overall Process	Stage I	Stage II	Stage III
27	$1.25 \pm 0.2$	$1.00 \pm 0.1$	$1.57 \pm 0.25$	$4.00 \pm 0.5$
40	$1.48 \pm 0.2$	$1.30 \pm 0.1$	$1.70 \pm 0.25$	$2.70 \pm 0.5$
50	$1.35 \pm 0.2$	$1.20 \pm 0.1$	$1.75 \pm 0.25$	$3.50 \pm 0.5$
60	$1.10 \pm 0.2$	$1.00 \pm 0.1$	$1.66 \pm 0.25$	$3.00 \pm 0.5$

**Table 8. Order of the chemical reaction for each stage of chemical transformation during rust removal by 3 vol% HEDPA at different solution temperatures.**

Solution Temperature ( C )	Order of the Chemical Reaction			
	Overall Process	Stage I	Stage II	Stage III
27	$1.28 \pm 0.2$	$1.09 \pm 0.1$	$1.62 \pm 0.25$	$3.60 \pm 0.5$
40	$1.65 \pm 0.4$	$1.40 \pm 0.2$	$1.68 \pm 0.25$	$3.20 \pm 0.5$
50	$1.30 \pm 0.2$	$1.40 \pm 0.1$	$2.20 \pm 0.25$	$4.00 \pm 0.5$
60	$1.26 \pm 0.2$	$1.00 \pm 0.1$	$1.80 \pm 0.25$	$3.50 \pm 0.5$

**Table 9. Order of the chemical reaction for each stage of chemical transformation during rust removal by 4 vol% HEDPA at different solution temperatures.**

Solution Temperature (C)	Order of the Chemical Reaction			
	Overall Process	Stage I	Stage II	Stage III
27	<b><math>1.25 \pm 0.2</math></b>	<b><math>1.20 \pm 0.1</math></b>	<b><math>1.67 \pm 0.25</math></b>	<b><math>4.01 \pm 0.5</math></b>
40	<b><math>1.46 \pm 0.2</math></b>	<b><math>1.80 \pm 0.1</math></b>	<b><math>1.50 \pm 0.25</math></b>	<b><math>3.70 \pm 0.5</math></b>
50	<b><math>1.39 \pm 0.2</math></b>	<b><math>1.26 \pm 0.1</math></b>	<b><math>1.95 \pm 0.25</math></b>	<b><math>4.50 \pm 0.5</math></b>
60	<b><math>1.20 \pm 0.2</math></b>	<b><math>1.09 \pm 0.1</math></b>	<b><math>1.36 \pm 0.25</math></b>	<b><math>3.60 \pm 0.5</math></b>

**Table 10. Order of the chemical reaction for each stage of chemical transformation during rust removal by 5 vol% HEDPA at different solution temperatures.**

Solution Temperature (C)	Order of the Chemical Reaction			
	Overall Process	Stage I	Stage II	Stage III
27	$1.12 \pm 0.2$	$1.22 \pm 0.1$	$1.47 \pm 0.25$	$3.85 \pm 0.5$
40	$1.18 \pm 0.2$	$1.60 \pm 0.1$	$1.30 \pm 0.25$	$3.70 \pm 0.5$
50	$1.39 \pm 0.2$	$1.32 \pm 0.1$	$1.57 \pm 0.25$	$3.50 \pm 0.5$
60	$1.35 \pm 0.2$	$1.60 \pm 0.1$	$1.86 \pm 0.25$	$4.12 \pm 0.5$

**Table 11. Order of the chemical reaction for each stage of chemical transformation during rust removal by 10 vol% HEDPA at different solution temperatures.**

Solution Temperature (C)	Order of the Chemical Reaction			
	Overall Process	Stage I	Stage II	Stage III
27	$1.05 \pm 0.2$	$1.40 \pm 0.1$	$1.77 \pm 0.25$	$3.88 \pm 0.5$
40	$1.12 \pm 0.2$	$1.37 \pm 0.1$	$1.38 \pm 0.25$	$3.25 \pm 0.5$
50	$1.25 \pm 0.2$	$1.29 \pm 0.1$	$1.82 \pm 0.25$	$3.16 \pm 0.5$
60	$1.00 \pm 0.2$	$1.99 \pm 0.1$	$2.06 \pm 0.25$	$3.60 \pm 0.5$

**Table 12. Order of the chemical reaction for each stage of chemical transformation during rust removal by 20 vol% HEDPA at different solution temperatures.**

Solution Temperature (C)	Order of the Chemical Reaction			
	Overall Process	Stage I	Stage II	Stage III
27	$1.05 \pm 0.2$	$1.60 \pm 0.1$	$1.88 \pm 0.25$	$3.76 \pm 0.5$
40	$1.18 \pm 0.2$	$1.36 \pm 0.1$	$1.29 \pm 0.25$	$3.25 \pm 0.5$
50	$1.15 \pm 0.2$	$1.23 \pm 0.1$	$1.35 \pm 0.25$	$3.51 \pm 0.5$
60	$1.30 \pm 0.2$	$1.07 \pm 0.1$	$1.66 \pm 0.25$	$3.52 \pm 0.5$

**Table 13. Order of the chemical reaction for each stage of chemical transformation during rust removal by 50 vol% HEDPA at different solution temperatures.**

Solution Temperature (C)	Order of the Chemical Reaction			
	Overall Process	Stage I	Stage II	Stage III
27	$1.03 \pm 0.2$	$1.12 \pm 0.1$	$1.47 \pm 0.25$	$4.09 \pm 0.5$
40	$1.40 \pm 0.2$	$1.23 \pm 0.1$	$1.76 \pm 0.25$	$3.79 \pm 0.5$
50	$1.45 \pm 0.2$	$1.60 \pm 0.1$	$1.57 \pm 0.25$	$3.90 \pm 0.5$
60	$1.00 \pm 0.2$	$2.00 \pm 0.1$	$1.96 \pm 0.25$	$3.86 \pm 0.5$

**Table 14. Order of the chemical reaction for each stage of chemical transformation during rust removal by 100 vol% HEDPA at different solution temperatures.**

Solution Temperature (C)	Order of the Chemical Reaction			
	Overall Process	Stage I	Stage II	Stage III
27	?	?	?	?
40	?	?	?	?
50	?	?	?	?
60	?	?	?	?

**Table 15 : The activation energy of rust removal process by HEDPA**

HEDPA Concentration (vol %)	Activation Energy (kcal/mole)
2	<b><u>11±1</u></b>
3	<b><u>12±2</u></b>
4	<b><u>14±2</u></b>
5	<b><u>19±2</u></b>
10	<b><u>27±5</u></b>
20	<b><u>30±5</u></b>
50	<b><u>2±1</u></b>
100	<b><u>0.2±0.3</u></b>

activation energy of the process. For example, if the concentration of HEDPA has increased from 4 to 5 vol%, the activation energy has increased by nearly 33 % and the rate of rust removal has a maximum activation energy of 30 kcal/mole at 20 vol.%.

Further increase in acid levels decreased the activation energy significantly.

A visual observation of the cleaned steel samples indicate that the samples treated with 2 – 4 vol.% HEDPA solution have a smooth surface texture while the samples treated with 10 – 20 vol% HEDPA has very rough surface with some ridges indicating a severe and non uniform dissolution of the rust and metal. Similarly, the rusted steel samples treated with 100 vol.% reagent were never free of rust even after prolonged treatment. It is possible that the rust removal process goes through a different mechanism.

Visually, it was observed that the sample rust is removed by 2 vol.% HEDPA solution at 25°C within 3 hours exposure. Gas ( $H_2$  assumed) evolution was evident within 30 minutes. Continued exposure beyond the three hour point resulted first in a gradual darkening of the surface and, depending on the solution conditions, a relatively thick, white to cream colored precipitation formed sometime between 10 and 24 hours on the sample surface as well as in solution. The collaborating researchers at the ANL have proposed a sequence of events related to the dissolution of iron oxide powders by HEDPA as follows: Figure 16 shows a schematic illustration of the sequence of possible chemical complex formation between HEDPA and FeO during chemical reaction. First the  $Fe^{2+}$  and /or  $Fe^{3+}$  may anchor to the two hydroxyl (OH groups) of the phosphate ion. After undergoing an internal rearrangement the reagent forms an

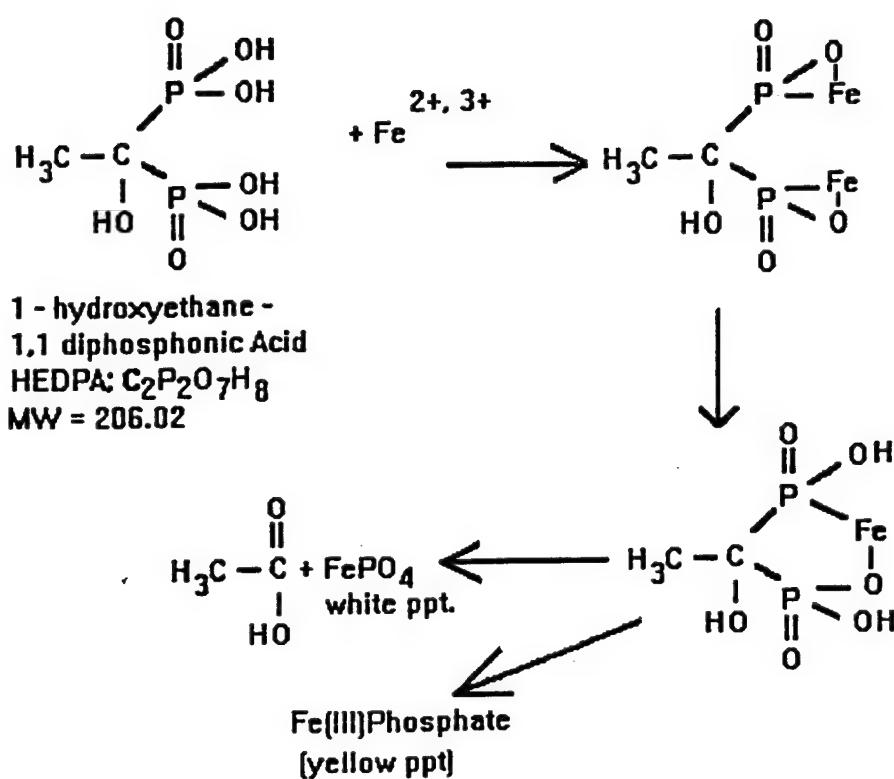
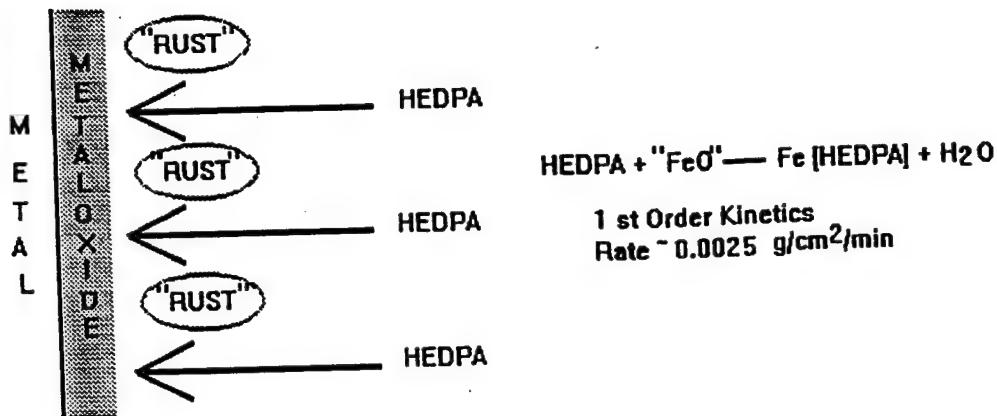
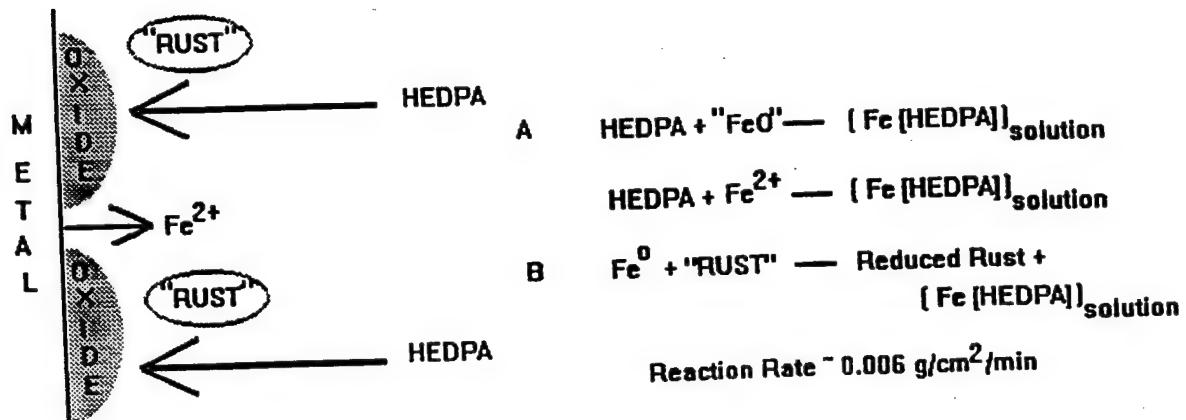


Figure 16. Schematic representation of typical chemical reaction product transformation during rust removal process by HEDPA.

## STAGE 1



## STAGE 2



## STAGE 3

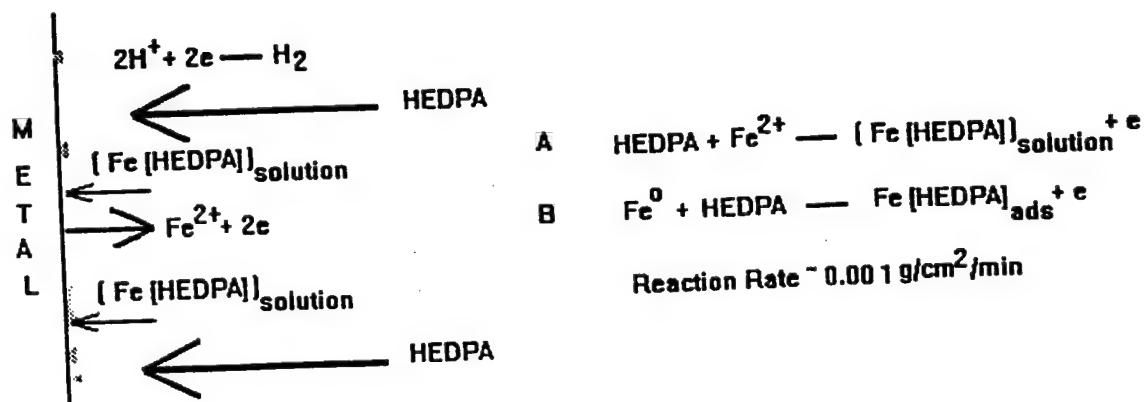
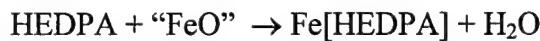


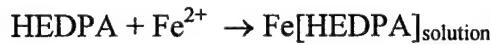
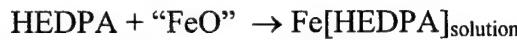
Figure 17. Schematic representation of possible mechanism for typical rust removal process by HEDPA.

intermediate iron HEDPA complex. This complex eventually breaks down to form acetic acid and FePO<sub>4</sub> (white precipitate) and or Fe (III) phosphate (yellow) precipitate.

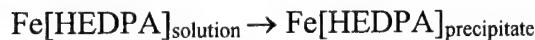
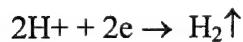
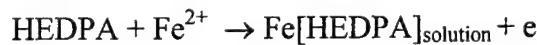
Assuming that the above mechanism may also apply to the rust removal from rusted steel surface, the stages involved in the cleaning of rusted steel samples can be suggested as follows: Figure 17 shows a schematic diagram of different stages involved in the rust removal process. In the first stage, the solid liquid interface consists of HEDPA and FeO and the reaction can be represented as



As the chemical reaction progresses and some FeO was dissolved by HEDPA, the base metal surface may also be exposed. The new solid – liquid interface thus may consist of [FeO, Fe] and HEDPA and the chemical reaction at the interface can be represented as



Continued dissolution of rust and some base metal by HEDPA exposes the base metal to the solid liquid interface thus initiating the H<sub>2</sub> gas evolution and eventual precipitation of Fe[HEDPA] precipitate in solution. The chemical reaction at the interface can be represented as



In order to establish an experimental support for the above suggested chemical process mechanism, two different investigative approaches were adopted. In the first set of experiments, the time for the formation of different precipitates was noted based on visual observation. In the second approach, a semi quantitative estimate for the maximum time required for transition between each chemical process was made based on classical solid state chemical kinetic model.

Tables 16 – 19 show the maximum time required for the complete transition between different stages of chemical reaction represented as a function of HEDPA concentration and the reaction temperature. The results indicate, that except for 2 vol. % HEDPA at 27 °C, there is no correlation between the theory and the experimental observation. These differences can be explained as follows: The present chemical kinetic model assumed that (i) the chemical process is independent of any diffusion controlled process; (ii) the chemical interactions are independent of temperature and (iii) the chemical reaction does not go through any intermediate chemical transformation (viz. A definite product is formed at any given instance).

A careful visual examination of the rust removal process revealed that at room temperature the initial precipitate would re-dissolve within the 24 hours resulting in a dark tea colored solution. A second precipitation would then occur during the third day's exposure and the chemical analysis suggested that the precipitate contain a mixture of complex higher order phosphates of iron. Based on the preliminary observations, a thorough chemical analysis was carried out. A brief qualitative description of the sequence of chemical events that were observed during a 72 hour study is given in

**Table 16. Maximum time required for complete transition between different stages of chemical reaction represented as a function of HEDPA concentration for rust removal at 27°C.**

HEDPA Concentration (vol.%)	Time for Changes from Different Stages of the Reaction (hour)					
	Stage I		Stage I – II		Stage I – II - III	
	(Obs.)	Max. Calc.	Obs.	Max. Calc.	Obs.	Max. Calc.
2	2.5		48	49	72	79
3	2		24	18	48	71
4	2		24?	12	48	51
5	1.5		6	6	24	53
10	1		6	4.5	24	18.5
20	1		3	2.0	24	13
50	2.5		24?	74(?)	48	-33(?)
100	?		24?	457(?)	48	144

**Stage I : Sample with rust - oxide is removed by HEDPA**

**Stage I – II : Sample has no oxide, metal is being removed and precipitate formed**

**Stage I – II – III : Sample is covered with thick precipitate and / or precipitates**

**Obs :** Visual observation during kinetic data measurement

**Max. Calc. :** Calculated using measured reaction rates. The theory assumes that the formation of precipitate goes through a maximum criticality for the process completion. (?) Error due to delay in observation and / or inadequate data)

**Table 17. Maximum time required for complete transition between different stages of chemical reaction represented as a function of HEDPA concentration for rust removal at 40°C.**

HEDPA Concentration (vol.%)	Time for Changes from Different Stages of the Reaction (hour)					
	Stage I		Stage I – II		Stage I – II - III	
	(Obs.)	Max. Calc.	Obs.	Max. Calc.	Obs.	Max. Calc.
2	2		4	29	6?	72
3	1.25		4	20	6?	35
4	0.75		3	15	4?	26
5	0.75		2	7.75	4?	16
10	0.5		1	4	2?	6
20	0.25		0.75	2.5	2?	3.5
50	0.75		1	20	2?	23
100	?		?	122	?	167

**Stage I : Sample with rust - oxide is removed by HEDPA**

**Stage I – II : Sample has no oxide, metal is being removed and precipitate formed**

**Stage I – II - III : Sample is covered with thick precipitate and / or precipitates**

**Obs :** Visual observation during kinetic data measurement

**Max. Calc. :** Calculated using measured reaction rates. The theory assumes that the formation of precipitate goes through a maximum criticality for the process completion. (?) Error due to delay in observation and / or inadequate data)

**Table 18. Maximum time required for complete transition between different stages of chemical reaction represented as a function of HEDPA concentration for rust removal at 50°C.**

HEDPA Concentration (vol.%)	Time for Changes from Different Stages of the Reaction (hour)					
	Stage I		Stage I – II		Stage I – II - III	
	(Obs.)	Max. Calc.	Obs.	Max. Calc.	Obs.	Max. Calc.
2	1.25		2.5	24	5?	63
3	0.75		2	9	5?	16
4	0.75		2	11	4?	9
5	0.5		1	3	3?	6.5
10	0.5		1	1	3?	1.2
20	0.25		0.5	0.5	1?	0.75
50	1		2	18	24	22
100	?		?	125	?	175

**Stage I : Sample with rust - oxide is removed by HEDPA**

**Stage I – II : Sample has no oxide, metal is being removed and precipitate formed**

**Stage I – II – III : Sample is covered with thick precipitate and / or precipitates**

**Obs :** Visual observation during kinetic data measurement

**Max. Calc. :** Calculated using measured reaction rates. The theory assumes that the formation of precipitate goes through a maximum criticality for the process completion. (? Error due to delay in observation and / or inadequate data)

**Table 19. Maximum time required for complete transition between different stages of chemical reaction represented as a function of HEDP concentration for rust removal at 60°C.**

HEDPA Concentration (vol.%)	Time for Changes from Different Stages of the Reaction (hour)					
	Stage I		Stage I – II		Stage I – II -III	
	(Obs.)	Max. Calc.	Obs.	Max. Calc.	Obs.	Max. Calc.
2	0.5		0.75	21	2 ?	?
3	0.5		0.75	5	2 ?	10
4	0.3		0.5	3	1 ?	5
5	0.25		0.5	1	1 ?	2.5
10	0.2		0.25	0.2	1 ?	0.4
20	0.2		0.5	0.25	?	?
50	0.5?		?	?	?	?
100	?		?	?	?	?

**Stage I : Sample with rust - oxide is removed by HEDPA**

**Stage I – II : Sample has no oxide, metal is being removed and precipitate formed**

**Stage I – II - III : Sample is covered with thick precipitate and / or precipitates**

**Obs :** Visual observation during kinetic data measurement

**Max. Calc. :** Calculated using measured reaction rates. The theory assumes that the formation of precipitate goes through a maximum criticality for the process completion. (?) Error due to delay in observation and/ or inadequate data)

Figure 18. The results suggest that there are at least 3 different precipitates that are formed during HEDPA – FeO/Fe interaction. Similarly, different solution color changes are noticeable for the HEDPA solution. For chemical analysis, all colored solutions were concentrated.

Figures 19 and 20 show typical x-ray diffraction patterns obtained from rusted steel and cleaned steel samples respectively. The results suggest that after the chemical treatment, some iron phosphate was formed or adsorbed on the surface as surface impurity. After nearly 6 hours of continuous chemical treatment with 2 vol% HEDPA, a white precipitate, which changed its color to green, was formed on the cleaned steel sample. Figure 21 shows the x-ray analysis of cleaned steel sample coated partially with a green precipitate. The results indicate that the cleaned steel surface is associated with complex mixture of higher order iron phosphates and some iron hydroxide.

Figures 22 - 24 show the x-ray diffraction patterns obtained from steel samples after 24, 48 and 72 hours of chemical treatment with 2 vol.% HEDPA. The results suggest that the sample surface is completely covered by the precipitate. The surface coverage is so thick that the incident x-ray cannot detect the steel surface. The results also suggest that after 24 hours, the precipitate has transformed primarily into iron pyrophosphate ( $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ ) and iron hydroxide ( $\text{Fe(OH)}_2$ ,  $\text{Fe(OH)}_3$ ). However, a continued chemical reaction re-dissolved the iron pyrophosphate ( $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ ) and iron hydroxide ( $\text{Fe(OH)}_2$ ,  $\text{Fe(OH)}_3$ ). After 48 hours, they are precipitated as a mixture of

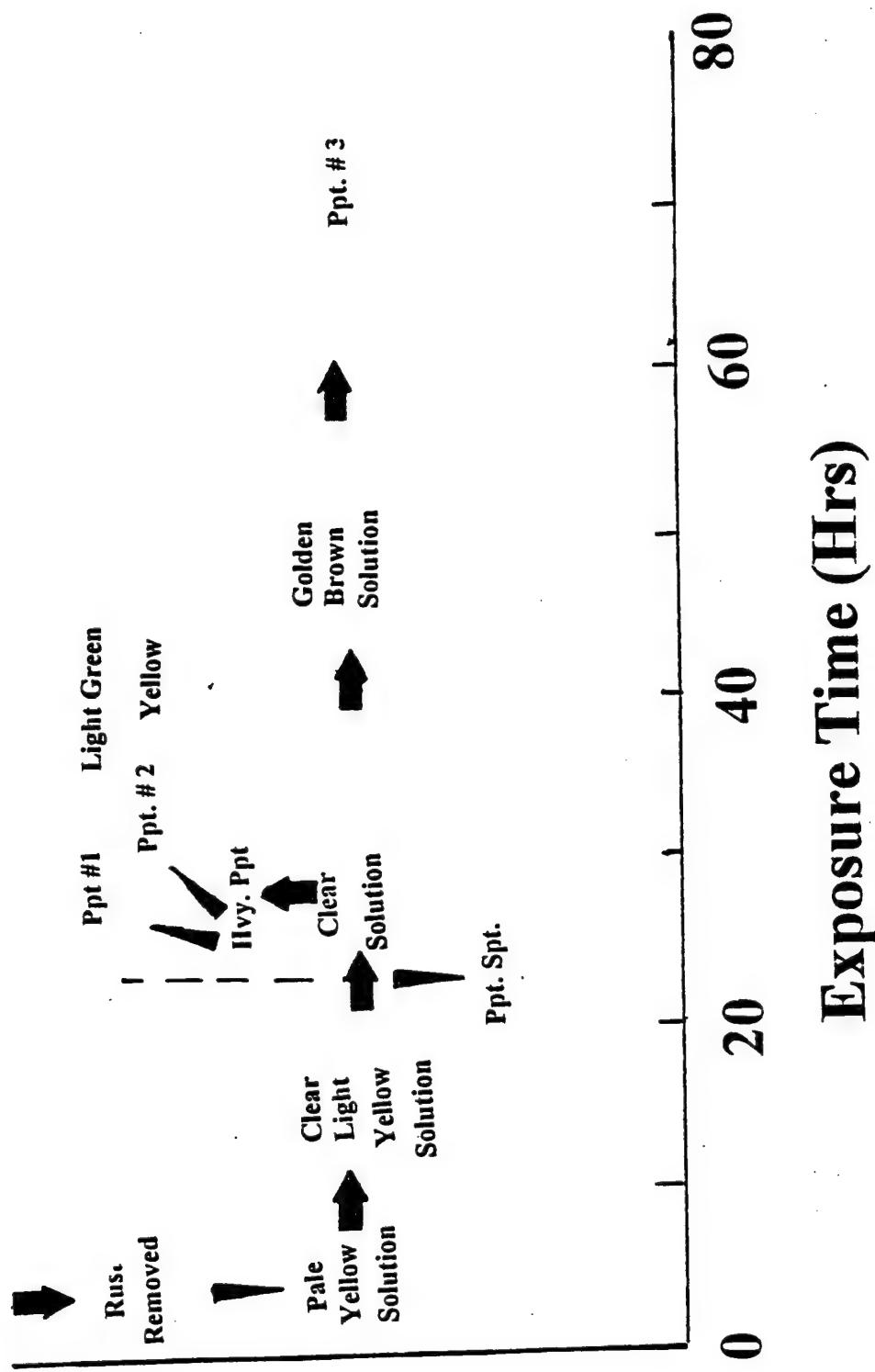


Figure 18. Visual characterization of sample surface and the solution phase during rust removal by 2 vol.% HEDPA at 27°C.

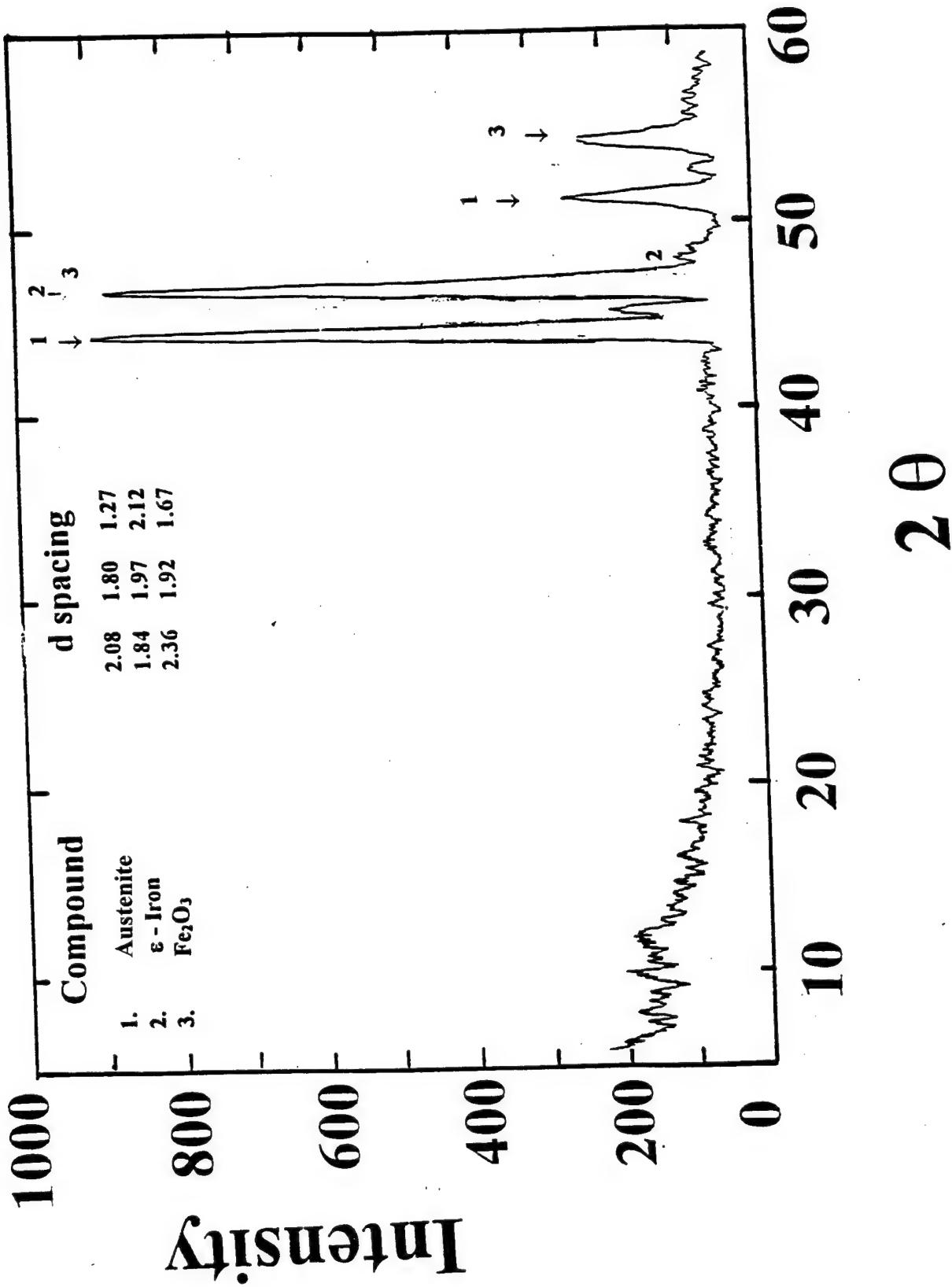


Figure 19. Typical x-ray diffraction obtained from rusted steel sample.

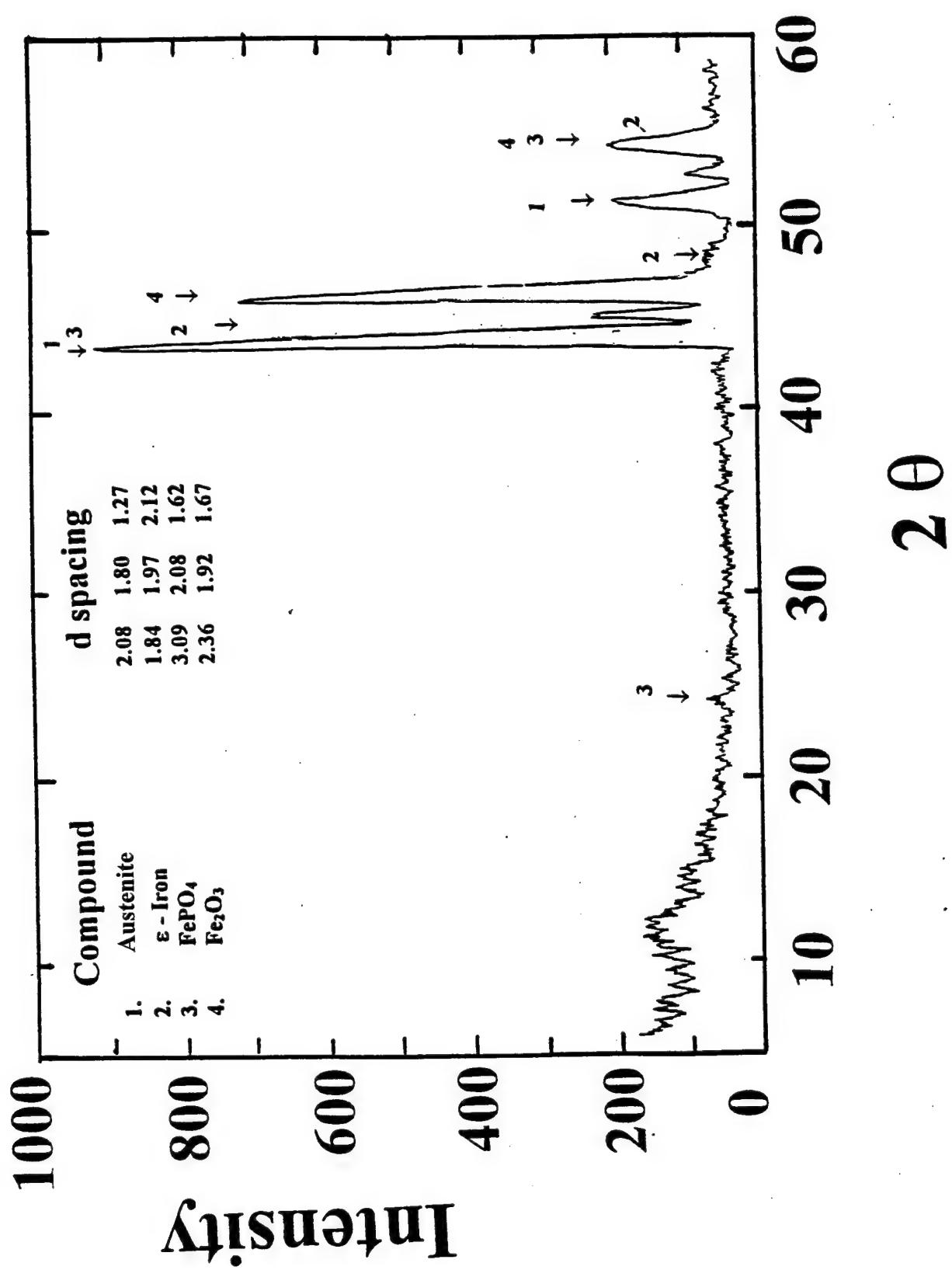


Figure 20. Typical x-ray diffraction obtained from cleaned steel sample coated after rust removal by 2 vol.% HEDPA at 27°C.

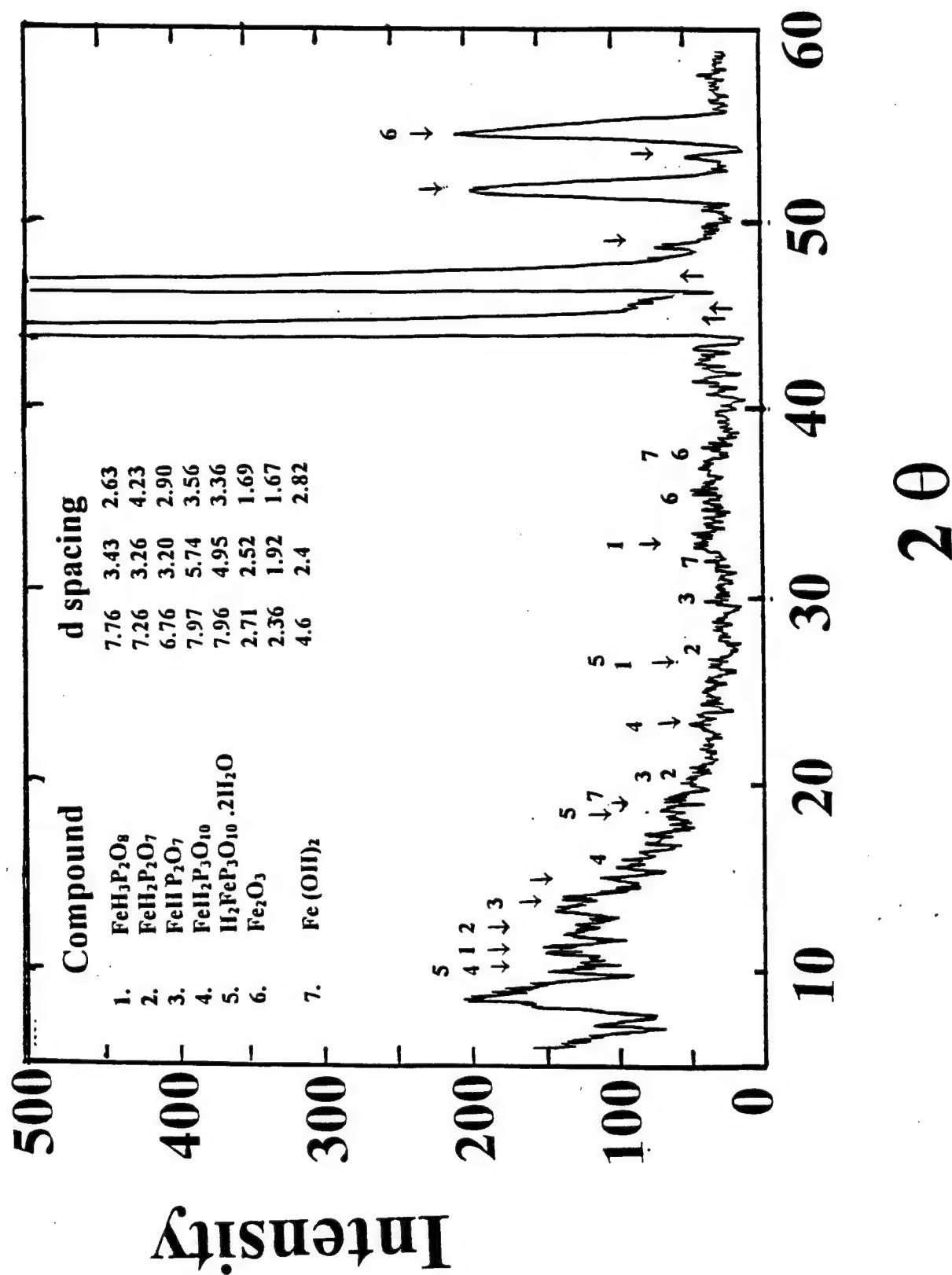


Figure 21. Typical x - ray diffraction obtained from cleaned steel sample coated with green precipitate (as a result of the re precipitation of reaction products) during chemical reaction with 2 vol.% HEDPA at 27°C.

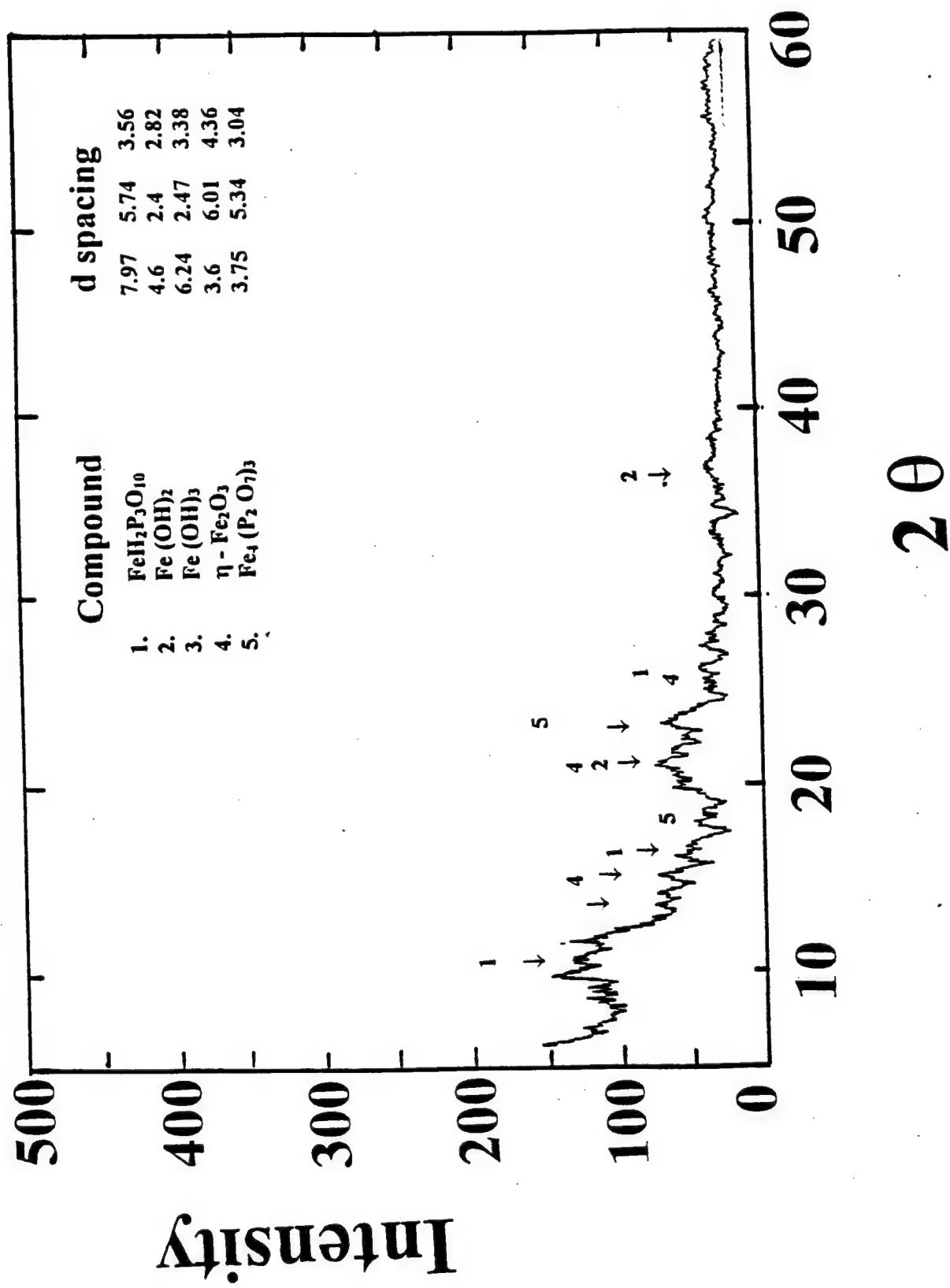


Figure 22. Typical x-ray diffraction obtained from golden yellow precipitate formed in solution (as a result of the re precipitation of reaction products) after 24 hours of chemical reaction with 2 vol.% HEDPA at 27°C.

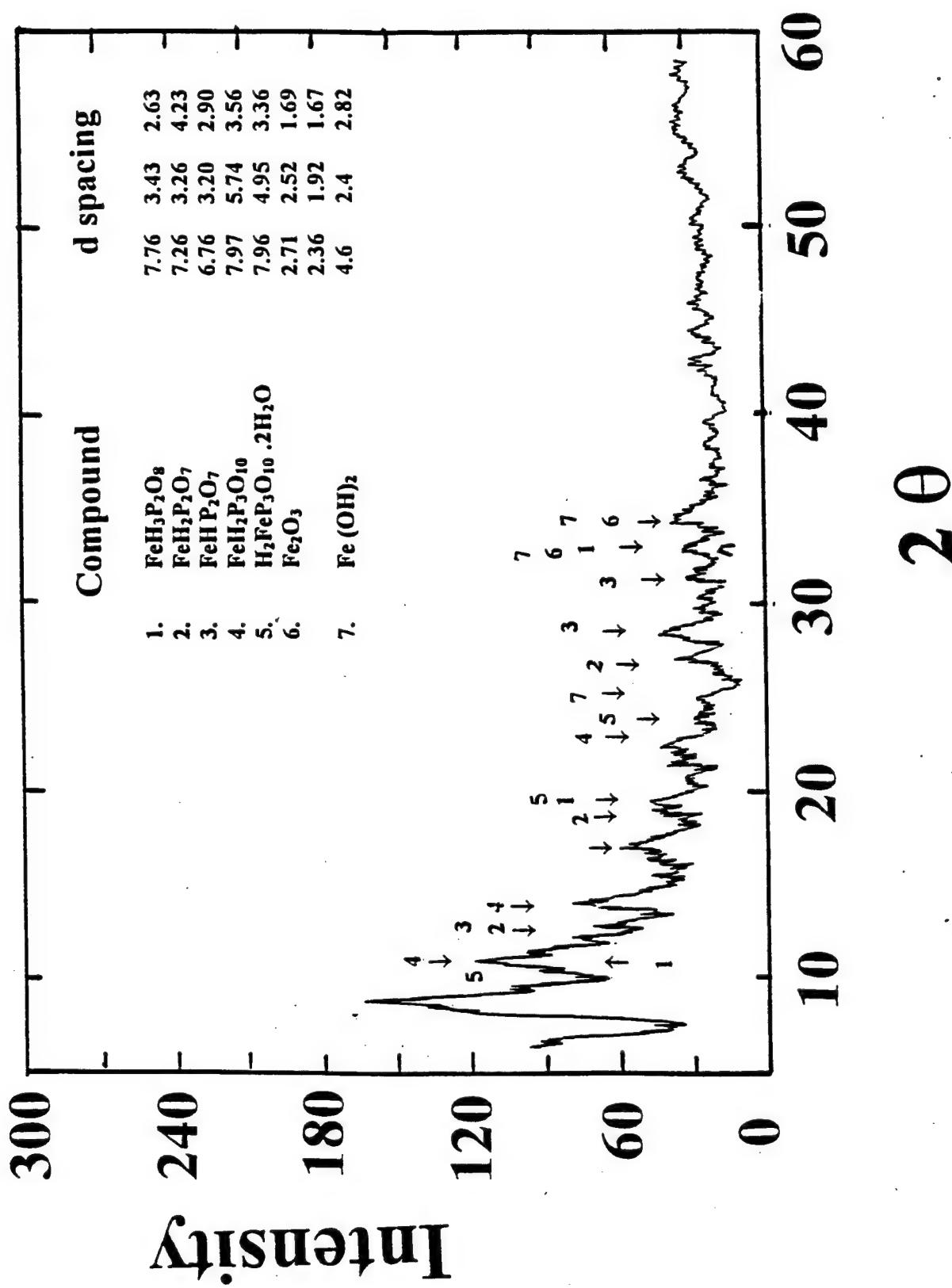


Figure 23. Typical x – ray diffraction obtained from dark yellow precipitate formed in solution (as a result of the re precipitation of reaction products) after 48 hours of chemical reaction with 2 vol.% HEDPA at 27°C.

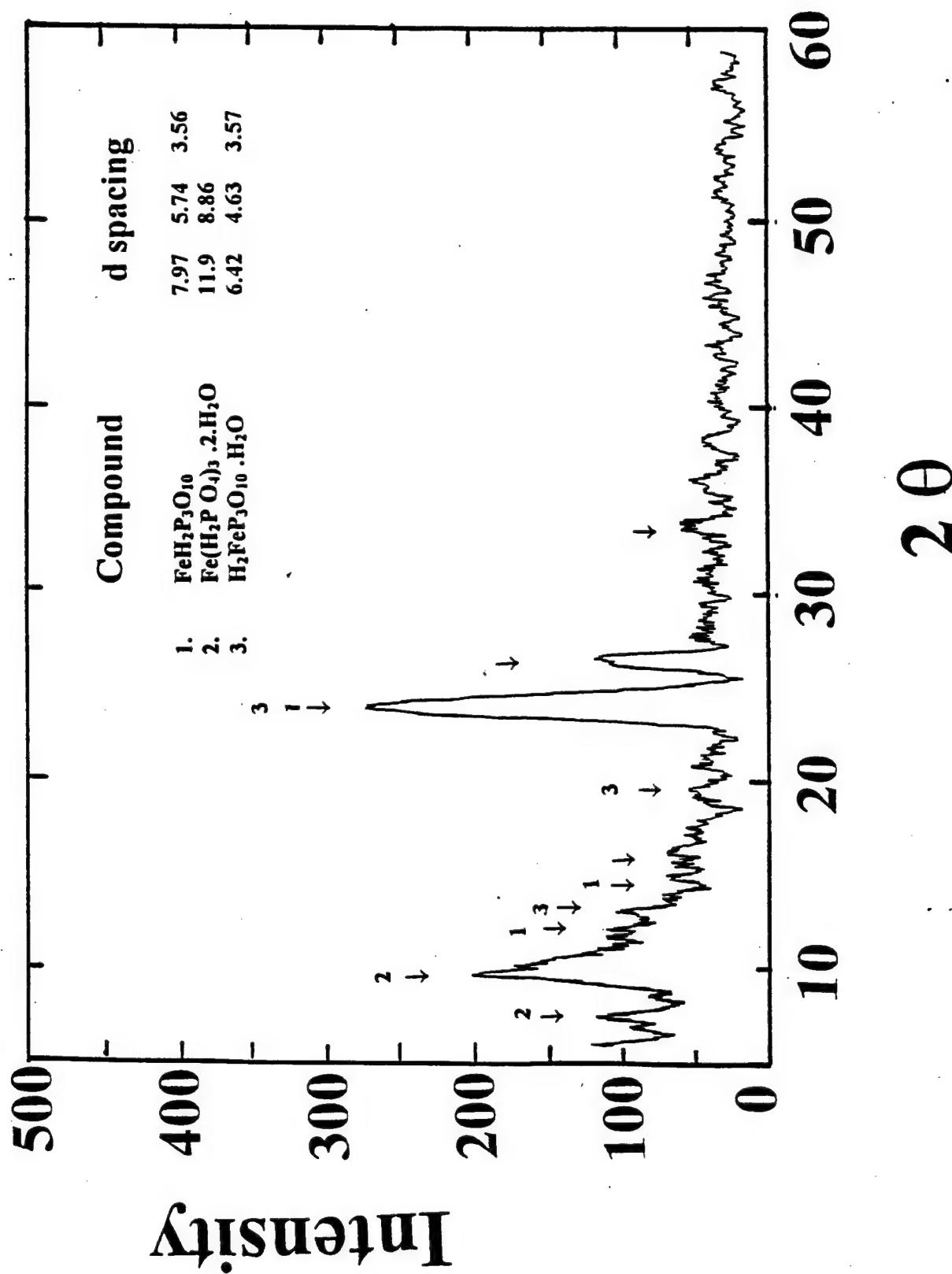


Figure 24. Typical x-ray diffraction obtained from yellow / brown precipitate formed in solution (as a result of the re precipitation of reaction products) after 72 hours of chemical reaction with 2 vol.% HEDPA at 27°C.

higher ordered iron phosphates that are similar to those formed initially (ie after 6 hours (Figure 21)); however, the crystal structure tend to change with time (Figure 24).

Figures 25-27 shows the structure of precipitates produced from HEDPA solution when the solution color changed to light yellow (after 6 – 9 hours), dark green brown (after 24 hours) and dark tea like brownish color (after 48 hours) respectively. The results suggest that the powders produced from all three colored solutions are nearly identical. All these powders have very fine crystallite structure. From the present results it can be postulated that once a certain critical crystallite size is achieved by the reaction products, they will re-precipitate from the solution onto the cleaned metal surface. A constant nucleation and adsorption onto the metal surface accelerates the crystallite growth.

### **SUMMARY AND CONCLUSION**

From the present investigation the following conclusions can be derived:

1. HEDPA is very effective in dissolving the rust. The rate of rust removal increases with an increase in the HEDPA concentration in the concentration range 2 – 20 vol.% and also with an increase in the reaction temperature 27 – 60°C. At higher HEDPA concentrations, the reaction kinetics were very slow.
2. The effective rust dissolution depends upon the acid concentration. While at lower concentration (< 5 vol.% HEDPA), the rust dissolution by HEDPA did not affect the surface morphology, very rough surface topography was created in samples treated with HEDPA in the concentration range 5 – 20 vol.%.

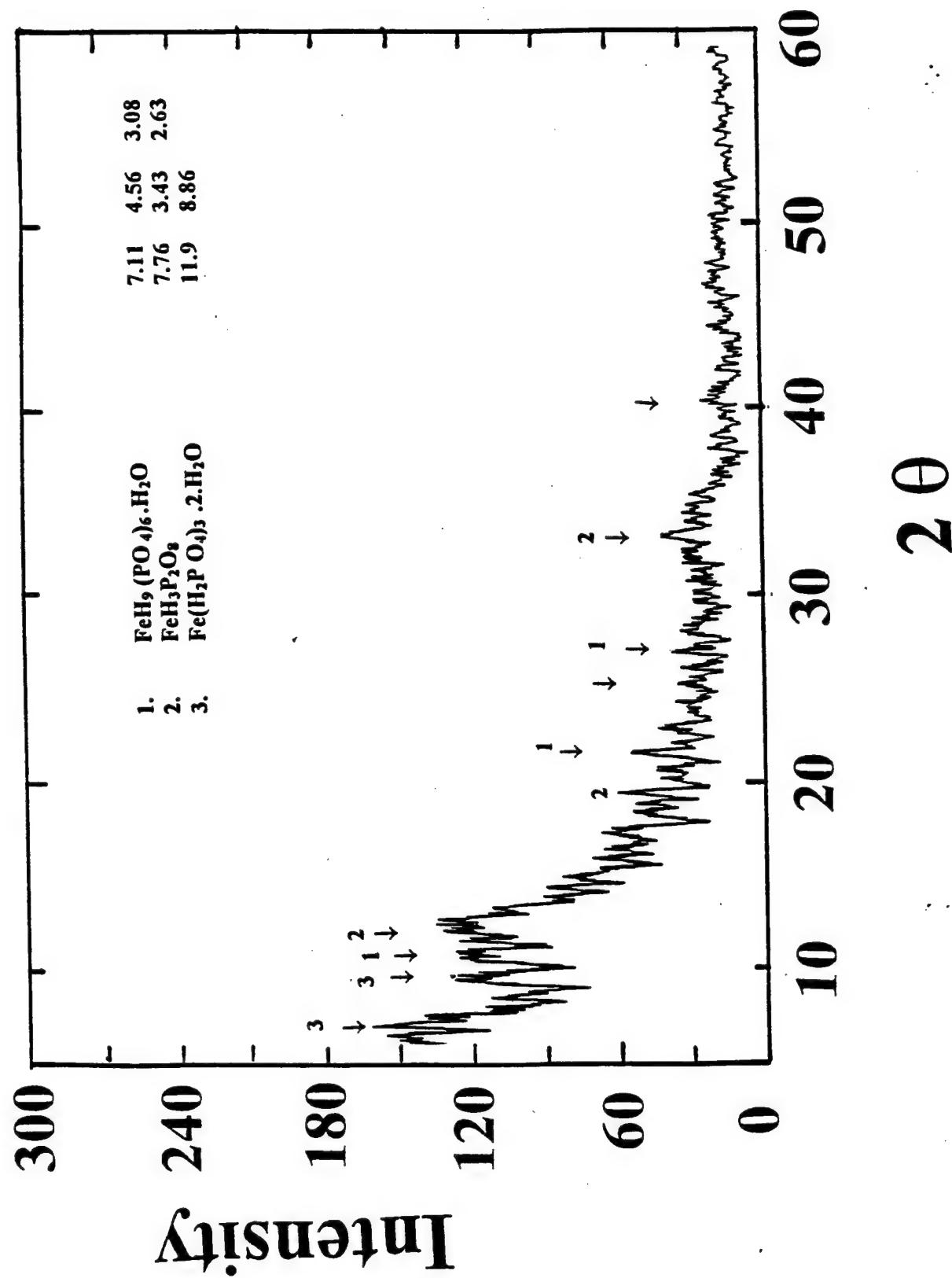


Figure 25. Typical x-ray diffraction of powder produced by concentrating 2 vol.% HEDPA after the solution color has changed to light yellow as a result of chemical reaction with rusted steel.

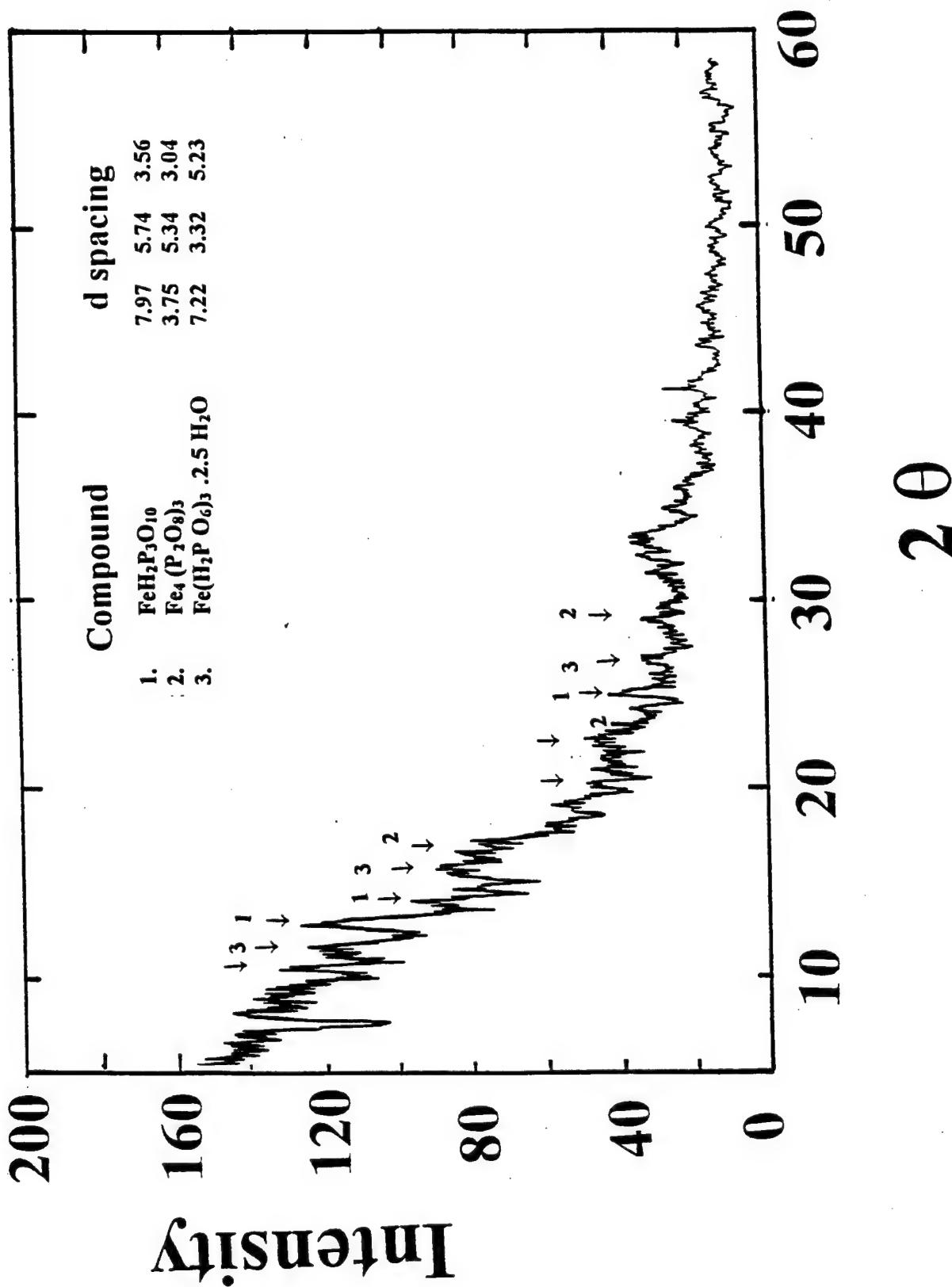


Figure 26. Typical X-ray diffraction of powder produced by concentrating 2 vol.% HEDPA after the solution color has changed to dark greenish brown as a result of chemical reaction with rusted steel.

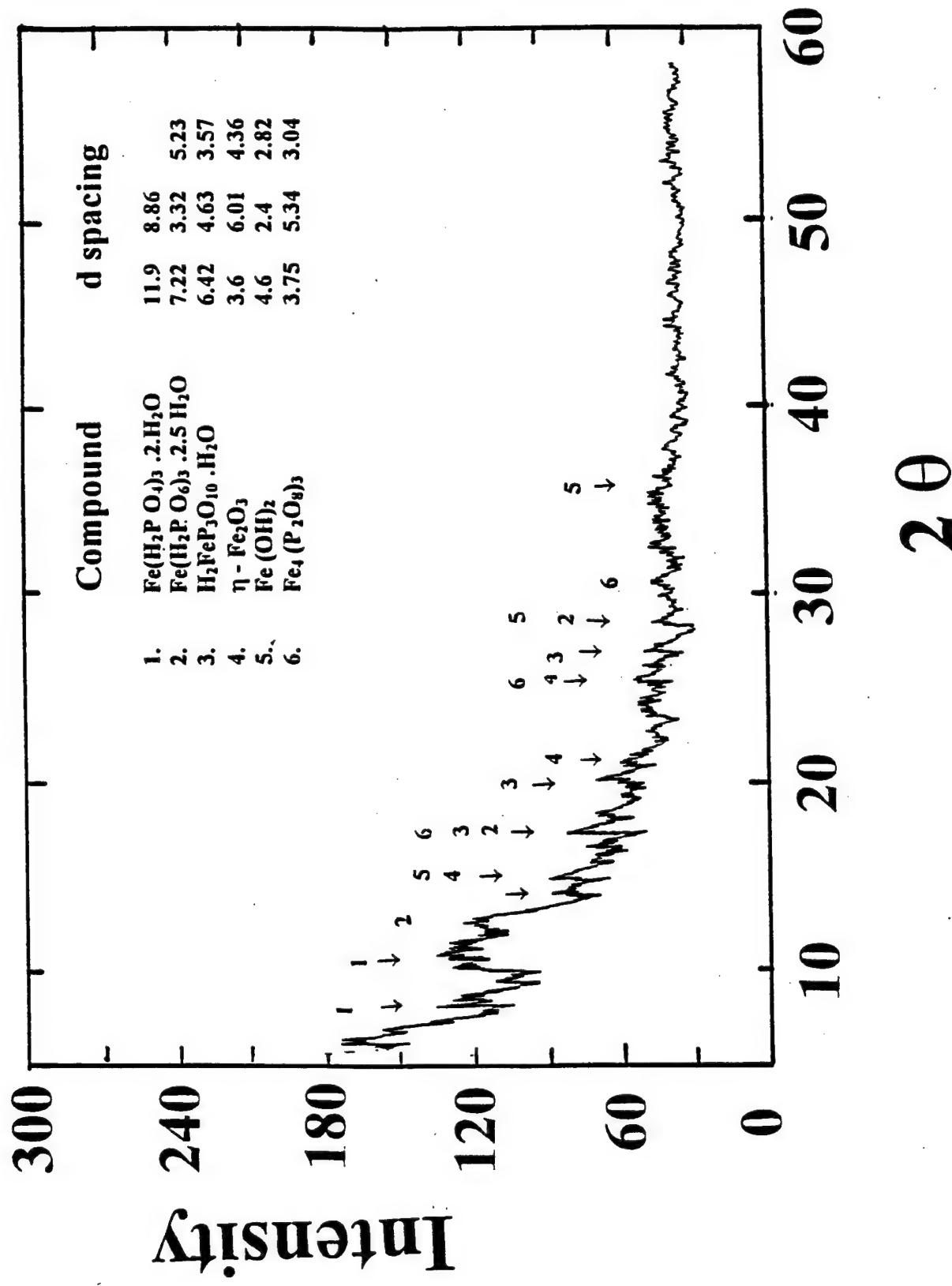


Figure 27. Typical x-ray diffraction of powder produced by concentrating 2 vol.% HEDPA after the solution color has changed to dark brown / tea color as a result of chemical reaction with rusted steel.

3. The mechanism of rust removal appears to be dependent on the HEDPA concentration. At lower concentration range ( 2- 4 vol%) the reaction process has an activation energy  $12 \pm 2$  kcal / mole. In the concentration range 10 – 20 vol.%, the process has an activation energy of 30 kcal/mole.
4. The rust removal process by HEDPA appears to be diffusion controlled. The kinetic rate parameters derived from the proposed model have to be redefined, taking the diffusion process into consideration.
5. The re-deposited precipitate, precipitate collapsed from solution, and the precipitate produced from solution are the same. However the crystallite size and crystal structure are different. While the precipitate re-deposited onto the cleaned steel sample have very well defined crystal structure, the precipitate produced from solution has very fine crystallite structure and the x-ray diffraction patterns show a mixture of crystal structure and the amorphous structure. The precipitate produced due to slow settlement from solution showed an intermediate crystal structure.
6. The reaction product is a mixture of several higher order iron phosphates. After 24 hours, it appears that except for the iron pyrophosphate, the other complexes re-dissolve in HEDPA. After 48 hours some of the dissolved compounds re-precipitate as iron pyrophosphate.
7. The precipitation, re-dissolution, re-precipitation continues and the iron pyrophosphate that settles after 72 hours has a very well defined crystal structure.

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## **REFERENCES**

1. Chiarizia, R. and E.P. Horowitz, *Hydrometallurgy*, 27, 339-360, 1991
2. Horowitz, E. P., Diamond, H., Gatrone, R. C., Nash, K. L. and Rickett, P. G., "Solvent Extraction," edt. T. Sekine, Pub. Elsevier Science, 1992.
3. Nash, K. L., *Radiochimica*, 54, 171-179, 1991.
4. Rao, A. S. and Murray, J.N., "Evaluation of Hydroxyethane Diphosphonic Acid (HEDPA) as Metal Cleaning Agent Using Chemical and Electrochemical Test Methods: Part I", Survivability, Structures and Materials Directorate, Naval Surface Warfare Center, Technical Report CARDIVNSWC-TR-61-98-16, June 1998.
5. Partridge, P. E., "Adaptability of Pipeline Decontaminated Procedures to Real Industry," P/N 98621, Corrosion 98, NACE Intl. Houston, TX, 1998.
6. Graedel, T.E. and R.P. Frankenthal; "Corrosion Mechanisms for Iron and Low Alloy Steels Exposed to the Atmosphere", *J. ECS*, 137, No. 8, pp 2385-2394, August 1990.
7. Surana, V. S. and Warren, H. J., *Trans. Inst. Min. Metallrg. Society*, C 28, 133-139, 1969.

8. Warren, I. H. and Devuyst, W., "Leaching of Metal Oxides," Proc. Int. Symp. On Hydrometallurgy, Pub. AIME, 229-264 (1973)
9. Cornell, R. M., Posner, A. M. and Quirk, J. P., J. Inorg. Nucl. Chem., 38, 563, 1976.
10. Osseo-Asare, K., "Interfacial Phenomena in Leaching Systems," Hydrometallurgical Process Fundamentals, edt. R. G. Bautista, Plenum Pub., New York, 227-268, 1982.
11. Nicol, M. J., "The Non-Oxidative Leaching of Oxides and Sulfides: An Electrochemical Approach," Hydrometallurgy Research, Development and Practice, eds. K. Osseo-Asare and J. D. Miller, Pub. AIME, New York, 177-195, 1982.

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